CR-128522

UNIVERSITY OF IDAHO

COLLEGE OF ENGINEERING
Engineering Experiment Station
Moscow, Idaho 83843

AN EQUATION OF STATE
FOR
OXYGEN AND
NITROGEN

R. B. Stewart
Professor and Chairman

R. T. Jacobsen
Assistant Professor

A. F. Myers
Research Engineer

Department of Mechanical Engineering

Research Report No. 13   October 1, 1971

-*i*-

ABSTRACT

Preliminary equations of state are presented for oxygen and nitrogen which provide accurate representations of the available P-ρ-T data for both fluids. The equation for nitrogen is applicable for temperatures from 70 K to 1300 K at pressures to 10,000 atmospheres, and the equation for oxygen for temperatures from 70 K to 323 K at pressures to 350 atmospheres. Deviations of calculated densities from representative experimental data are included. A volume explicit equation of state for oxygen to be used in estimating density values in the range of applicability of the equation of state is also presented.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

I   INTRODUCTION

The equation of state for oxygen published in [1]* has been employed in both pre-mission and mission support activities in the Apollo program. In addition, to accurately account for venting rates in the analysis of the oxygen and nitrogen systems for the Skylab program, vapor pressure equations and specific heat values will be required along with the equation of state. With the advent of the two-gas atmosphere used in the Skylab program it will be necessary to perform the same type of calculations on both oxygen and nitrogen systems.

Prior to this project, the NASA Consumables Analysis Section used the equation of state for oxygen from [1] in computer models of the oxygen systems. In September, 1971, an equation of state for nitrogen was published by Coleman and Stewart [2,3] which had essentially the same form as that used for oxygen by Stewart [1], and this equation was adopted for nitrogen system calculations.

The objective of the project which is the subject of this report, is to determine improved equations of state for nitrogen and oxygen, using the same form of the equation for both fluids. The improvements that are to be considered include the following:

1.   The accuracy of the equation of state for oxygen will be improved by incorporating the new P-ρ-T data including all published high temperature data and other thermodynamic data which have been published subsequent to the completion of [1] in the determination of the coefficients for the new equation.

2.   The study of the functional form of the equations of state to improve their accuracy for nitrogen and oxygen will be continued. The equations of state for both will be of the same form, and consequently these studies will be carried on for both fluids simultaneously.

3.   Other thermodynamic data will be considered in the determination of accurate equations of state, with the goal of publishing equations of state for oxygen and nitrogen which are sufficiently accurate to represent not only the P-ρ-T surface, but also other thermodynamic data (e.g., entropy, enthalpy, heat capacity, velocity of sound data).

---

* Numbers in brackets refer to references at the end of this report.

4. The accuracy of other thermodynamic relationships for oxygen and nitrogen employed in the calculation of thermodynamic property tables (i.e., equations for the vapor pressure and the ideal gas heat capacity) will also be improved.

5. The range of values to be covered by these thermodynamic property table formulations shall include the entire range of pressures and temperatures for which data are available, as well as extrapolations which theory indicates are prudent for higher temperatures and lower pressures for the vapor.

II STATUS OF OXYGEN AND NITROGEN EQUATIONS OF STATE, JUNE 30, 1971

A. The Thermodynamic Properties of Oxygen

In 1966, R. B. Stewart, then with the National Bureau of Standards, Cryogenic Data Center, published his Ph.D. thesis [1]. This publication was based on preliminary results of the oxygen properties measurement program of the NBS Cryogenics Division and other data from the scientific literature. Thermodynamic property tables based on NBS measurements were subsequently published [4]. The mathematical formulation used by NBS for calculation of these thermodynamic tables was selected to provide the most accurate representation of the data, but the calculation procedure is not well suited for computer applications in thermodynamic modeling and simulation. The equation of state developed by Stewart, however, is well suited for systems calculation by computer, and produces thermodynamic property values nearly equivalent to the property tables published by the NBS. The following table is reprinted from [5], and serves as a guide to the advantages of three alternate methods for thermodynamic property formulations (the reference numbers in this table have been added as examples of these methods).

Table I
Comparison of Calculation Methods for Computer Analysis

Type of Program	Speed	Versatility	Accuracy
Equation of State [1,2]	Medium	Best	Medium
Tab Code [6]	Best	Very Little	Medium
Multifunction [4]	Slow	None	Best

Stewart's equation of state was completed prior to the publication of the NBS measurement program. Subsequently, P-ρ-T measurements were made by NBS of the liquid below the normal boiling point and around the critical point which have not been incorporated into Stewart's equation of state. NBS has also completed measurements of constant volume heat capacity (C_v) which may be used to improve the oxygen properties formulations. With the inclusion of these additional data sets in the determination of the equation of state, it is expected

that the limitations in Stewart's work, which were due to a scarcity of measured values, may now be corrected and the accuracy of all of the derived thermodynamic properties calculated using the equation of state will be improved. (Reference [1] includes graphical illustrations and discussions of the accuracy of the equation of state and the thermodynamic property formulations using the equations presented.)

In addition to the equation of state, the work of Stewart [1] also included equations for the ideal gas heat capacity and the vapor pressure. These equations should now be revised. The ideal gas heat capacity values were based on the tables from [8]. A recent tabulation of ideal gas properties by Baehr [9] provides new values based on recent molecular constants, and this equation should now be fit to the newer values.

The vapor pressure equation in [1] was based on the data by [10], which were inadequate to describe the vapor pressure below 80 K. A new vapor pressure equation recently completed in a separate study at the University of Idaho was published in [11]. This equation is based on the newer vapor pressure data from [12], and on heat capacity measurements for the saturated liquid [13], as well as the older data from [10].
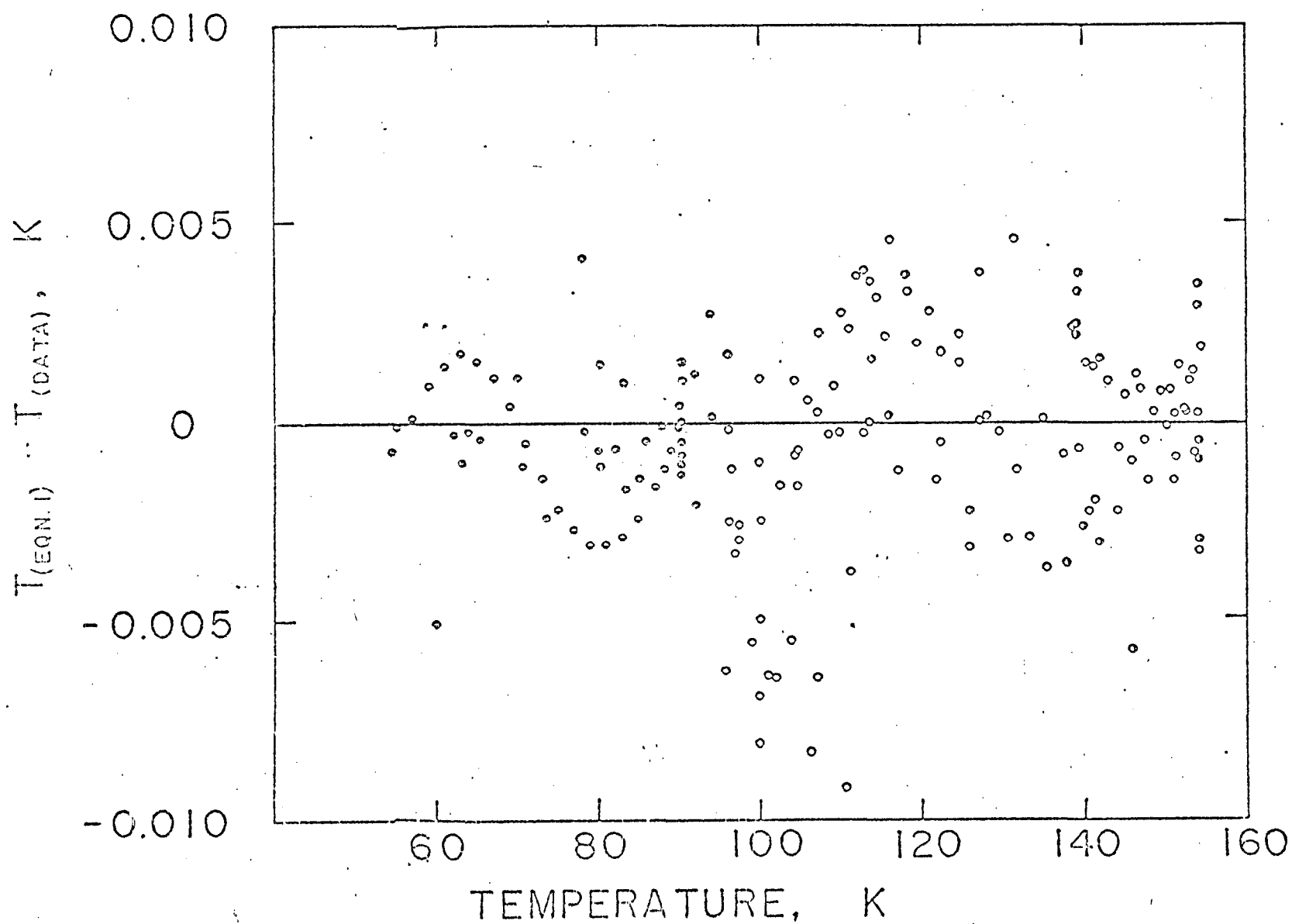
The vapor pressure equation from [11] is,

$$\ln P = \frac{A_1}{T} + A_2 + A_3 T + A_4 (T_c - T)^\alpha + A_5 T^3 + A_6 T^4 + A_7 \ln T \tag{1}$$

where the A_i are the coefficients given in Table II, with T the temperature in degrees Kelvin, T_c = 154.581 K (the critical temperature), and P the pressure in atmospheres.

Table II

Coefficients for Vapor Pressure Equation (1) for Oxygen
Reprinted from [11]

A_1 = -0.9841114846 x 10^3	A_5 = -0.1046194284 x 10^{-5}
A_2 = -0.1156470767 x 10^2	A_6 = -0.5657508967 x 10^{-9}
A_3 = 0.5933202019 x 10^{-1}	A_7 = 0.3343730069 x 10
A_4 = 0.9855772473 x 10^{-3}	α = 1.915755272

A comparison of temperatures calculated from equation (1) and the data used to determine the coefficients of equation (1) is given in figure 1.

Figure 1 Deviations of Calculated Temperatures from Data used in Fit of Oxygen Vapor Pressure Equation

HOGE [10] ○   VALUES FROM C_σ DATA [13] ○

WEBER [0-1] ○   MUIJLWIJK ET AL. [12] ○

B. The Thermodynamic Properties of Nitrogen

A two year study of the thermodynamic properties of nitrogen by Dr. Stewart and co-workers has produced an equation of state, a vapor pressure equation, and an equation for the ideal gas heat capacities, which are used for the calculation of thermodynamic property tables. This work was sponsored by the NBS Office of Standard Reference Data, and the results are published in [7]. The following is extracted, in part, from [7].

The form of the equation of state developed for nitrogen is,

$$
\begin{aligned}
P = \rho RT \\
+ \rho^2 (N_1 T + N_2 T^{\frac{1}{2}} + N_3 + N_4/T^{\frac{1}{2}} + N_5/T + N_6/T^2 + N_7/T^3 + N_8/T^4) \\
+ \rho^3 (N_9 T^2 + N_{10} T + N_{11} + N_{12}/T + N_{13}/T^2) \\
+ \rho^4 (N_{14} T + N_{15}) \\
+ \rho^5 (N_{16} + N_{17}/T) \\
+ \rho^3 (N_{18}/T^2 + N_{19}/T^3 + N_{20}/T^4) \exp(-\gamma\rho^2) \\
+ \rho^5 (N_{21}/T^2 + N_{22}/T^3 + N_{23}/T^4) \exp(-\gamma\rho^2) \\
+ \rho^7 (N_{24}/T^2 + N_{25}/T^3 + N_{26}/T^4) \exp(-\gamma\rho^2) \\
+ \rho^9 (N_{27}/T^2 + N_{28}/T^3 + N_{29}/T^4) \exp(-\gamma\rho^2) \\
+ \rho^{11} (N_{30}/T^2 + N_{31}/T^3 + N_{32}/T^4) \exp(-\gamma\rho^2) \\
+ \rho^{13} (N_{33}/T^2 + N_{34}/T^3 + N_{35}/T^4) \exp(-\gamma\rho^2)
\end{aligned}
\tag{2}
$$

where the N_i are the coefficients given in Table III, with T the temperature in degrees Kelvin, P the pressure in atmospheres, and ρ the density in moles/liter. These coefficients, except the value of γ in the exponential terms, were determined by a least squares fit to the weighted data.

The equation of state (2) represents the entire range of P-ρ-T values for nitrogen which have been measured, to approximately the uncertainty of the data. This includes values for the liquid near the triple point and along the saturated liquid boundary, for the liquid at the freezing line, and for the gas from 80 to 1273 K, with pressures to 10,000 atm.

Figures 2 to 22 illustrate the deviation between selected measurements of the density and values calculated by the equation of state (2), (i.e., the percent density deviation, $[(\rho_{exp} - \rho_{calc})/\rho_{exp}] \times 100$, where ρ_{exp} represents the observed density reported by the experimenter, and ρ_{calc} the density calculated from equa-

Table III

Coefficients for the Equation of State (2) for Nitrogen
Reprinted from [7]

N_1 = 0.442846853539105 x 10^{-2}

N_2 = -0.829417233959518 x 10^{-1}

N_3 = 0.831816820844281

N_4 = 0.789454995207039 x 10^{1}

N_5 = -0.519464730111641 x 10^{3}

N_6 = 0.486788204145566 x 10^{5}

N_7 = -0.276765813270827 x 10^{7}

N_8 = 0.531902528027746 x 10^{8}

N_9 = -0.107038956039902 x 10^{-6}

N_{10} = 0.274500963709232 x 10^{-3}

N_{11} = -0.911499335271588 x 10^{-1}

N_{12} = 0.145051669173734 x 10^{2}

N_{13} = 0.277646315858169 x 10^{3}

N_{14} = -0.458649005760810 x 10^{-6}

N_{15} = 0.138049438981636 x 10^{-2}

N_{16} = 0.821404094790335 x 10^{-4}

N_{17} = -0.986881710201094 x 10^{-2}

N_{18} = 0.137925677998808 x 10^{3}

N_{19} = -0.111691086112682 x 10^{6}

N_{20} = 0.131992876308097 x 10^{7}

N_{21} = -0.107110551745687 x 10^{2}

N_{22} = -0.280710075038644 x 10^{3}

N_{23} = 0.103571934551340 x 10^{6}

N_{24} = -0.324638262862371 x 10^{-2}

N_{25} = -0.143915062954146 x 10^{1}

N_{26} = 0.232500139742939 x 10^{3}

N_{27} = -0.201017505855138 x 10^{-3}

N_{28} = 0.283301453486397 x 10^{-1}

N_{29} = -0.255833003328750 x 10^{1}

N_{30} = 0.126004937195284 x 10^{-6}

N_{31} = -0.159463113142953 x 10^{-4}

N_{32} = 0.294340278758674 x 10^{-2}

N_{33} = -0.246822376653425 x 10^{-9}

N_{34} = 0.784099910579200 x 10^{-8}

N_{35} = -0.108263295098092 x 10^{-5}

γ = 0.0056

R = 0.0820535 liter-atm/mol·K

tion (2) for each experimental pressure and temperature). The temperatures for which these comparisons are given were selected to afford a representative analysis of the available data, and to cover the range of temperatures for which data are available. The following comments are made with regard to the comparisons in figures 2 to 22.

The data for the low temperature liquid are illustrated on the graphs for 77 K, 90 K, and 120 K to 123 K. The data of Van Itterbeek and Verbeke [N-32, N-33] for temperatures of 65.85 K, 72.31 K, and 77.89 K are generally in agreement with the equation; however, systematic deviations from the equation are found for these data at 77.31 K, 84.99 K, and 90.60 K. It appears that the data reported by Van Itterbeek and Verbeke are not a self-consistent set of values. The data by Streett and Staveley [N-28] deviate from the equation systematically at lower temperatures as indicated by the graphs at 77 K and 90 K; however, their data beginning with temperatures of 105 K and above are generally in agreement with the equation, to the extent illustrated at 120 K to 123 K. Liquid data by Weber [N-35] are illustrated for approximate isochoric values ranging from 11 to 28 moles/liter in figure 22. (Weber's measurements were made using an approximately constant mass-constant volume system for integral values of temperature, and each isochor represents an experimental run.) These data are more precise than the other liquid data, and there is a systematic deviation from the equation. However, a more meaningful evaluation is obtained by considering the deviations for values at the same temperature, rather than for the same experimental run. (The lowest and highest temperature for each isochor are shown in figure 22.) It is estimated that the equation of state for the low temperature liquid has an uncertainty of ± 0.5%.

The data near the critical point are illustrated for temperatures from 125 K to 128 K. This is an experimentally difficult region for precise measurements, and the imprecision of the data is evident. The region near the critical point is also a difficult region for fitting the equation of state, and systematic deviations between the equation and the data resulting from fitting problems near the critical point appear to be present for isotherms above the critical point; e.g., as illustrated in figures 6 and 7 for 133 K and 143 K.

The lack of concordance between the data sets above 1000 atm. is particularly notable. In general, the equation of state fits the data of Saurel [N-26] and Robertson and Babb [N-25], which were judged to be the most accurate. The data by Malbrunot and Vodar [N-19] and by Malbrunot [N-20] are not in accord with the selected data; and in addition to this lack of concordance, inconsistencies between these two documents (which are assumed to contain the results of the same experiment) raise some question as to the experimenters' own convictions regarding the accuracy of their measurements.

, The coefficients of the equation of state were determined by a least squares fit of the weighted data indicated in Table IV. As noted in this table, the data of the saturated liquid states (i.e., on the vapor pressure line [N-11, N-29], and the freezing line [N-13]) were not used in determining these coefficients. These values were excluded since the data reported are temperature and density, and the pressure is determined from an independent measurement of the vapor pressure or freezing pressure. It is, therefore, of particular interest to note the extrapolation of the equation of state from the single phase region to these saturation boundaries. These comparisons are given in figures 23 and 24.

The deviations of the equation of state from liquid P-ρ-T data at the vapor pressure are systematic, and are generally negative, (i.e., the calculated densities are greater than the measured values). It is expected that a new fit of the equation of state including these saturation data would reduce the magnitude of the deviations. The fit of the equation of state reported here did not incorporate the saturated liquid data since the use of these values is dependent upon the vapor pressure equation, and comparisons between vapor pressure measurements and vapor pressure calculated from the equation of state (i.e., by equating Gibbs function, pressure and temperature) should be made before introducing the saturated liquid values into the fit. (This is being done as a part of the continuing studies.)

A comparison of the equation of state to liquid density data on the freezing line also indicates systematic deviations. It is anticipated that a more critical evaluation of the liquid P-ρ-T data may be afforded after a comparison of heat capacity data. (This evaluation is included as a part of the continuing studies.)

Table IV

10

SUMMARY OF P-V-T DATA FOR NITROGEN

Source	Temperature Range (K)	Pressure Range (atm)	Number of Data Points	Uncertainty in Density
Amagat [N-1]	273 - 473	1 - 3000	149	*
Bartlett [N-2]	273	1 - 1000	9	*
Bartlett et al. [N-3]	273 - 673	1 - 1000	52	*
Bartlett et al. [N-4]	203 - 293	100 - 1000	42	.2 %
Benedict [N-5]	90 - 273	99 - 1500	25	.3 %
Benedict [N-6]	98 - 473	981 - 5879	124	.3 %
Canfield [N-7]	133 - 273	2 - 300	152	.15%
Crain et al. [N-8]	143 - 273	2 - 500	70	.1 %
Friedman [N-9]	80 - 300	1 - 200	201	.1 %
** Gibbons [N-10]	72 - 77	22 - 124	17	.15%
† Goldman, Scrase and Cockett [N-11]	78 - 125	1 - 32	80	*
** Golubev and Dobrovolskii [N-12]	78 - 133	49 - 484	53	.1 %
†† Grilly and Mills [N-13]	64 - 120	76 - 3441	10	*
Hall [N-14]	103 , 113	2 - 9	8	{ .55% at 113 K .39% at 103 K
Heuse and Otto [N-15]	273	0.04 - 0.1	8	*
Holborn and Otto [N-16]	273 - 673	24 - 100	66	*
Holborn and Otto [N-17]	273 - 403	20 - 100	24	.05%
Kammerlingh Onnes and van Urk [N-18]	124 - 293	30 - 50	143	*
Malbrunot and Vodar [N-19]	473 - 1273	1000 - 4000	63	*
Malbrunot [N-20]	473 - 1273	800 - 5000	191	*
Michels et al. [N-21]	273 - 423	20 - 80	56	.01%
Michels et al. [N-22]	273 - 423	200 - 3000	147	{ .1 % above 1000 atm .01% below 1000 atm
Miller, Stroud, and Brandt [N-23]	21	9 - 260	10	.1 %
Otto, Michels and Wouters [N-24]	298 - 423	45 - 400	63	.01%
Robertson and Babb [N-25]	308 - 673	1600 - 10,000	170	.05%
Saurel [N-26]	423 - 1073	10 - 900	37	.1 %
Smith and Taylor [N-27]	273 - 473	34 - 319	40	*
** Streett and Staveley [N-28]	77.35 - 120.23	4.32 - 680.46	107	.1 %
† Terry et al. [N-29]	77 - 104	1 - 10	15	*
Tsiklis and Polyakov [N-30]	294 - 673	1600 - 10,000	69	1 %
Tsiklis [N-31]	323 - 423	3000 - 6000	21	1 %
** Van Itterbeek and Verbeke [N-32,N-33]	65 - 90	15 - 840	80	.1 %
Verschoyle [N-34]	273 - 293	25 - 205	36	*
** Weber [N-35]	80 - 140	30 - 266	76	.15%

* Data sets used in comparisons but not in fit.
** Liquid data.
† Saturated liquid data.
†† Liquid on freezing line.

The vapor pressure equation (1) from [11] with T_c = 126.2 K should now be used for nitrogen. The coefficients from a least squares fit to the data of Armstrong [N-36] and Weber [N-35] are presented in Table V.

Table V

Coefficients for Vapor Pressure Equation (1) for Nitrogen,
Reprinted from [7]

A_1 = -0.6129036050 x 10 ^{3} A_5 = -0.4376881279 x 10^{-5}

A_2 = -0.6558840929 x 10 ^{2} A_6 = 0.5270751218 x 10^{-9}

A_3 = 0.9971628689 x 10^{-1} A_7 = 0.1447693081 x 10 ^{2}

A_4 = 0.2471462741 x 10^{-2} α = 1.95

A comparison of the vapor pressure equation with the selected data sets used in determining the coefficients is given in figure 25.
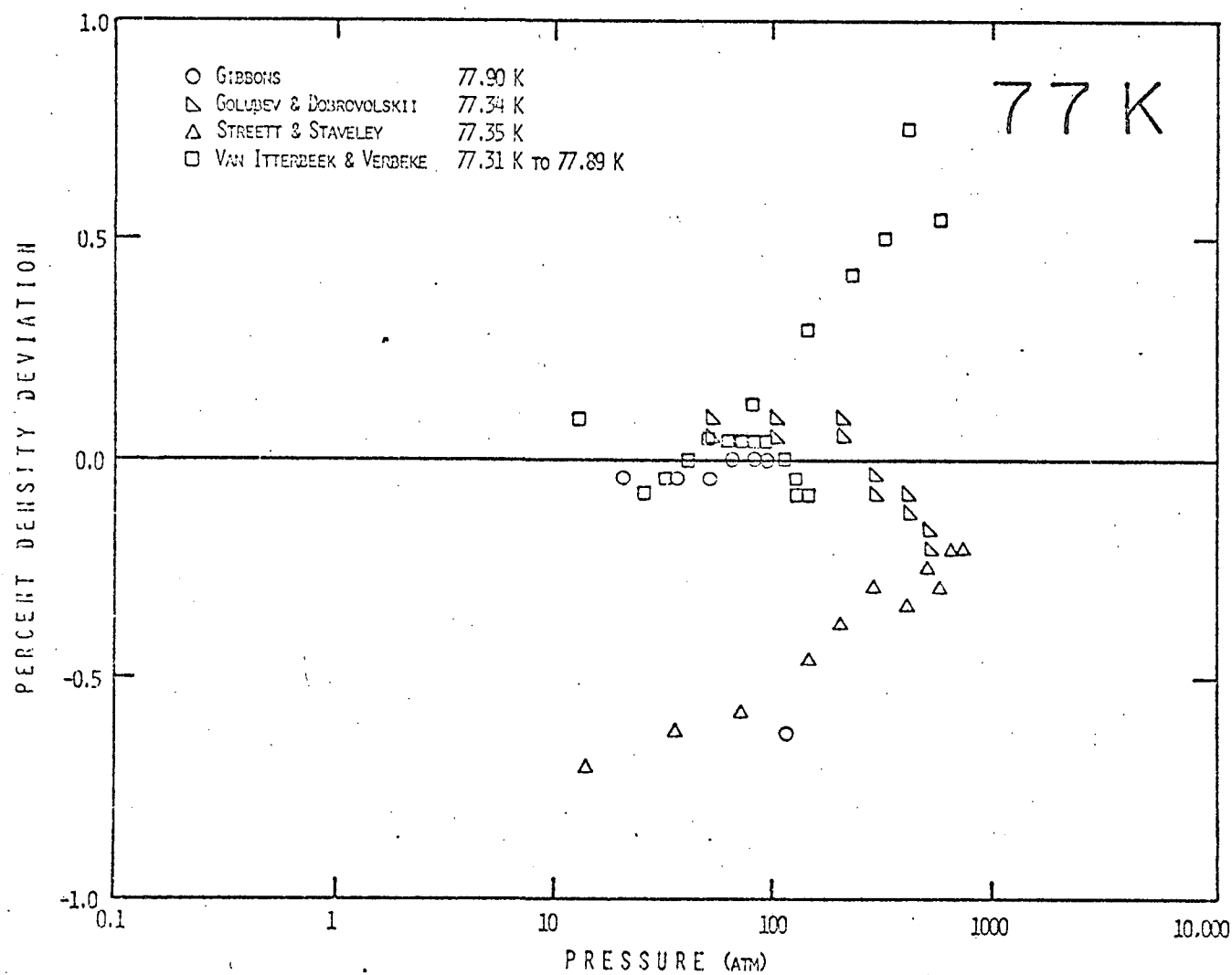
Figure 2   Deviations in Density of Equation (2) from the
Experimental Data of [N-10, N-12, N-28, N-32, N-33].
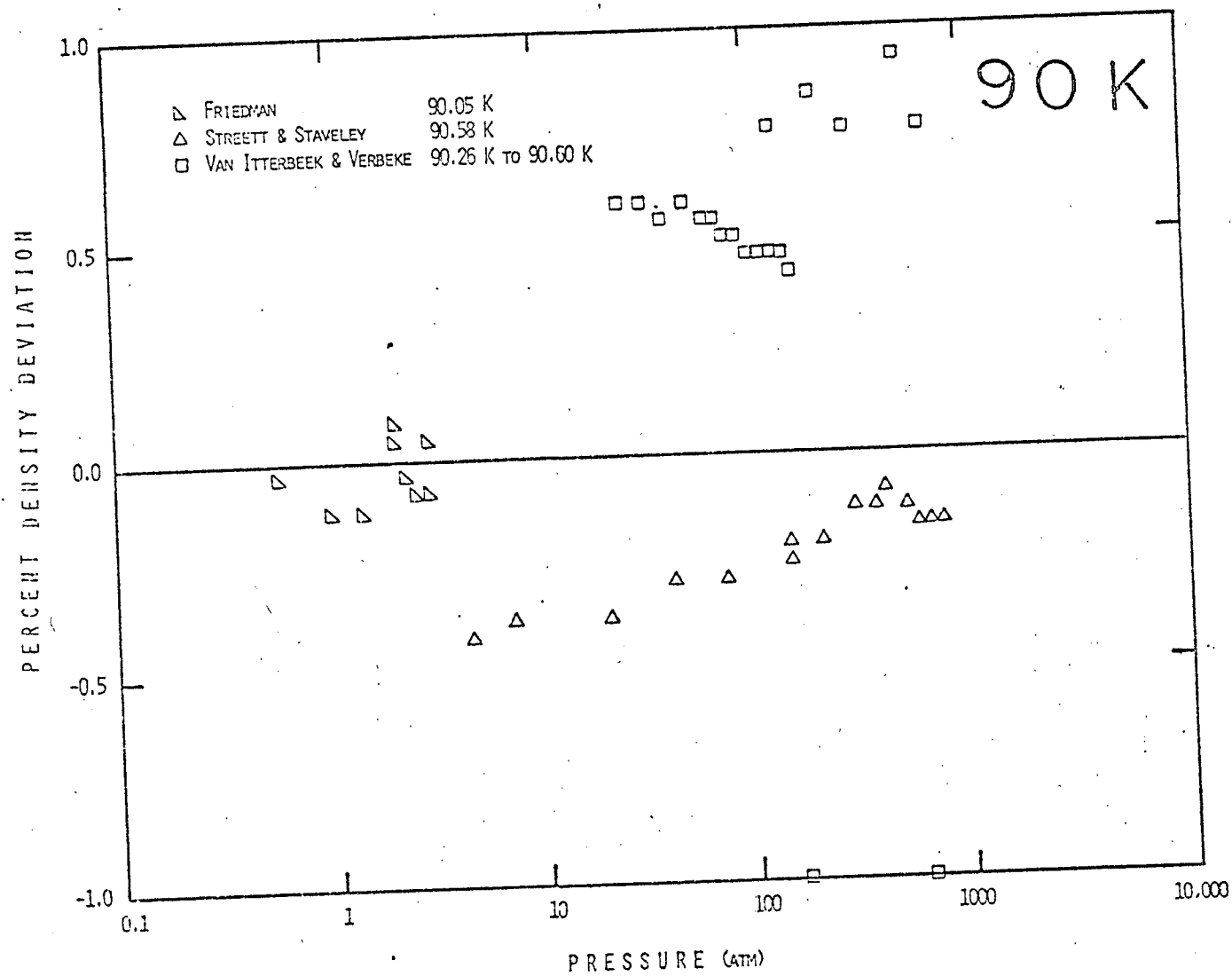
Figure 3 Deviations in Density of Equation (2) from the
Experimental Data of [N-9, N-28, N-32, N-33].
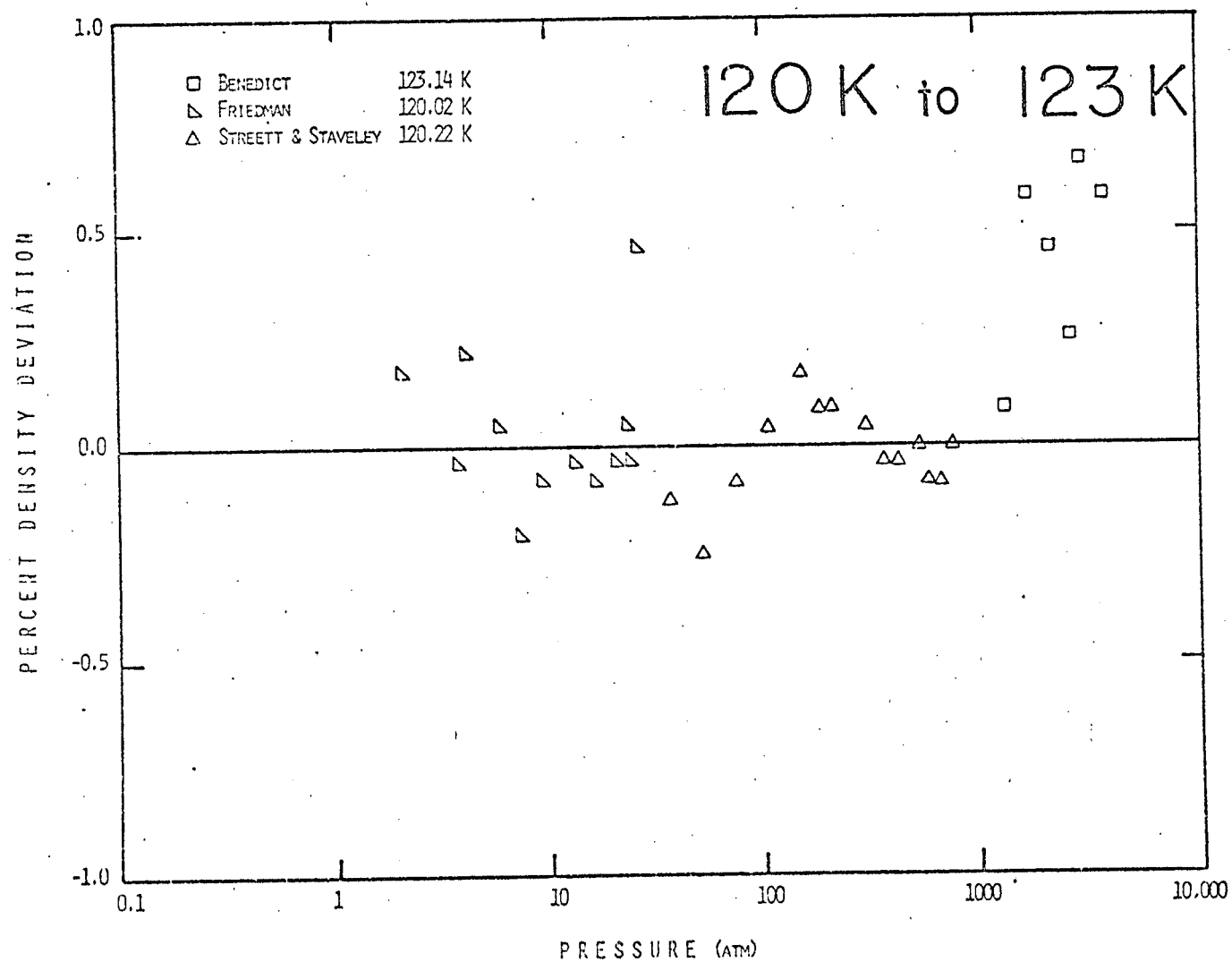
Figure 4 Deviations in Density of Equation (2) from the
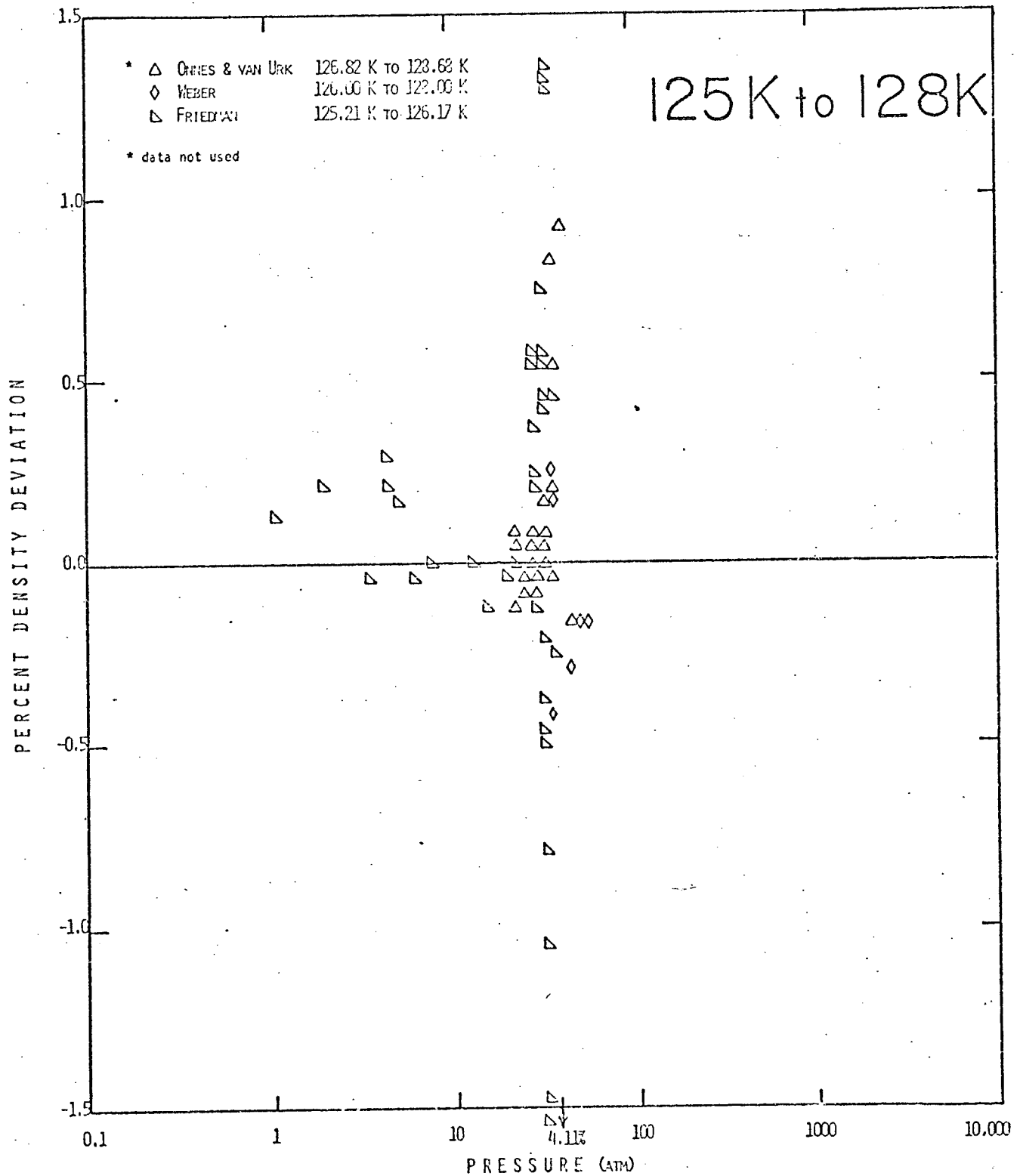Experimental Data of [N-6, N-9, N-28].

Figure 5 Deviations in Density of Equation (2) from the
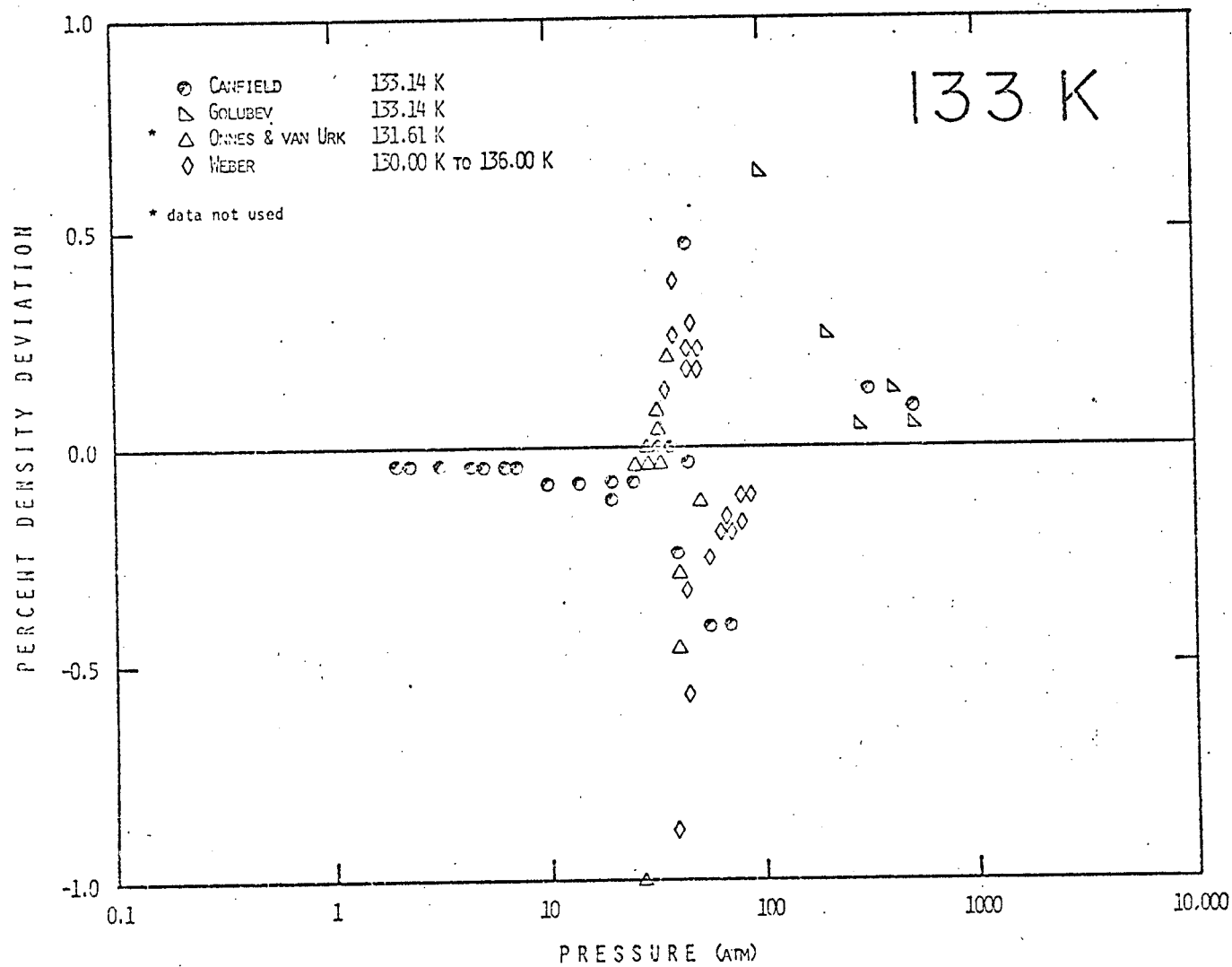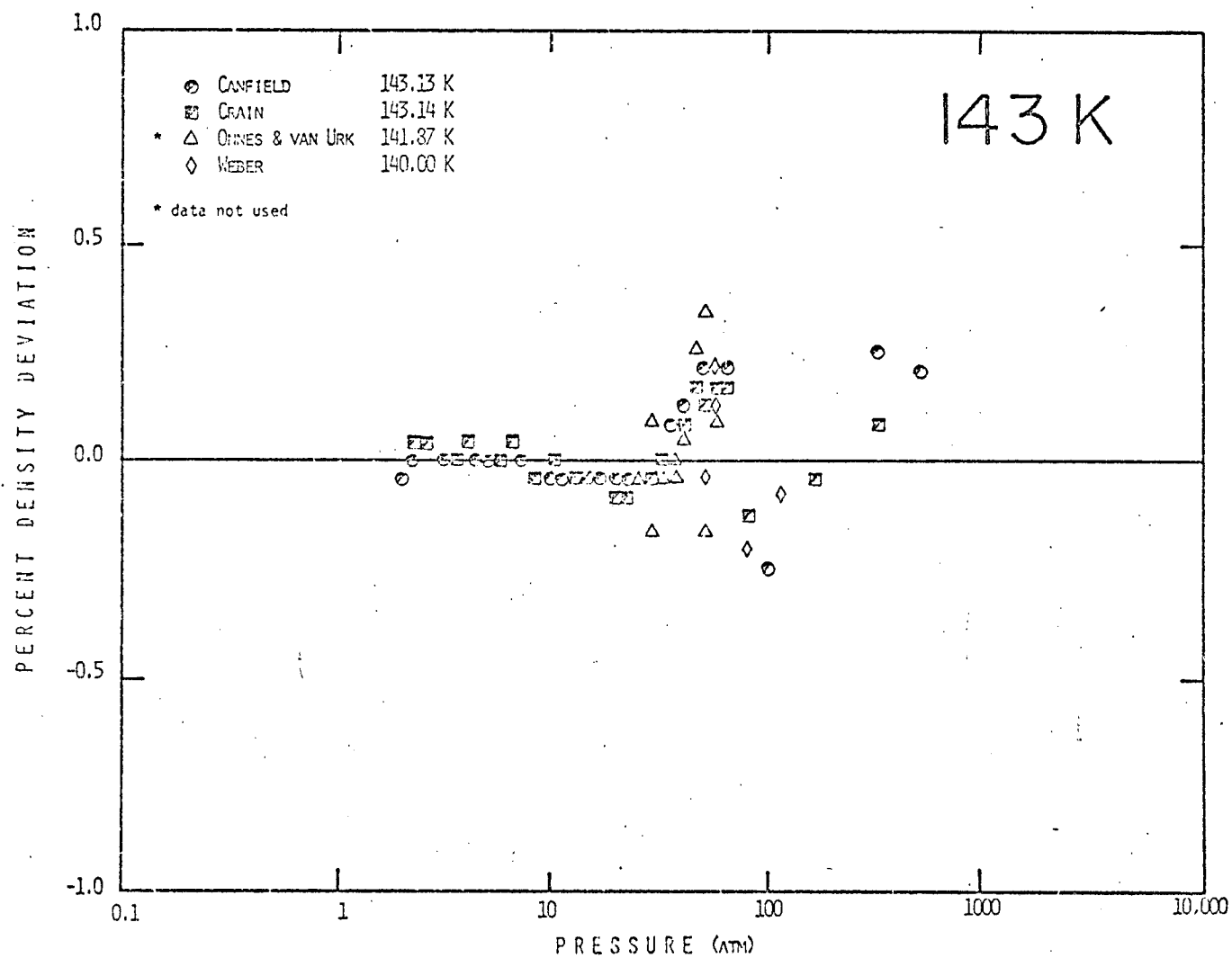Experimental Data of [N-18, N-35, N-9].

Figure 6 Deviaticns in Density of Equation (2) from the
Experimental Data of [N-7, N-12, N-18, N-35].

Figure 7   Deviations in Density of Equation (2) from the
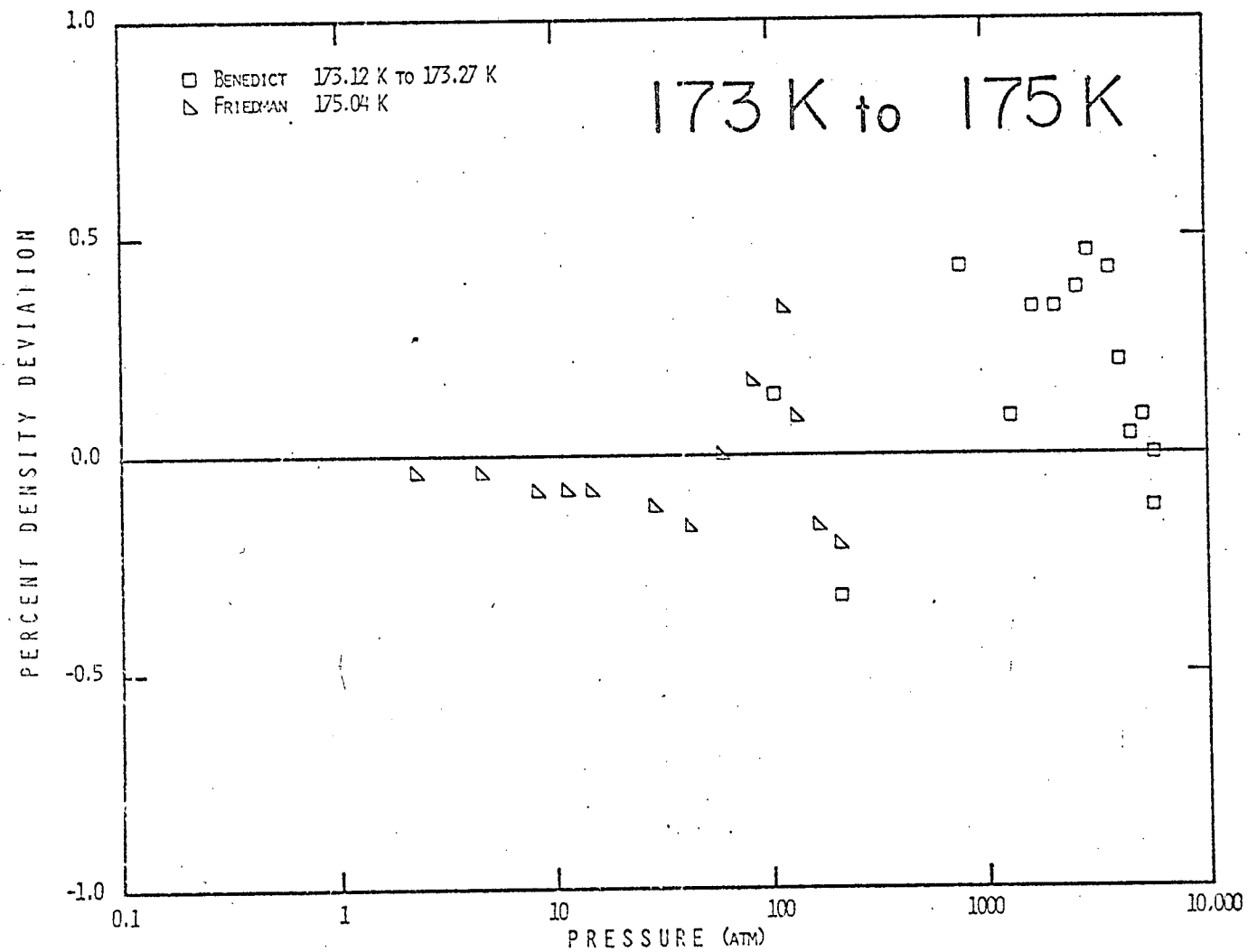Experimental Data of [N-7, N-8, N-18, N-35].

Figure 8   Deviations in Density of Equation (2) from the
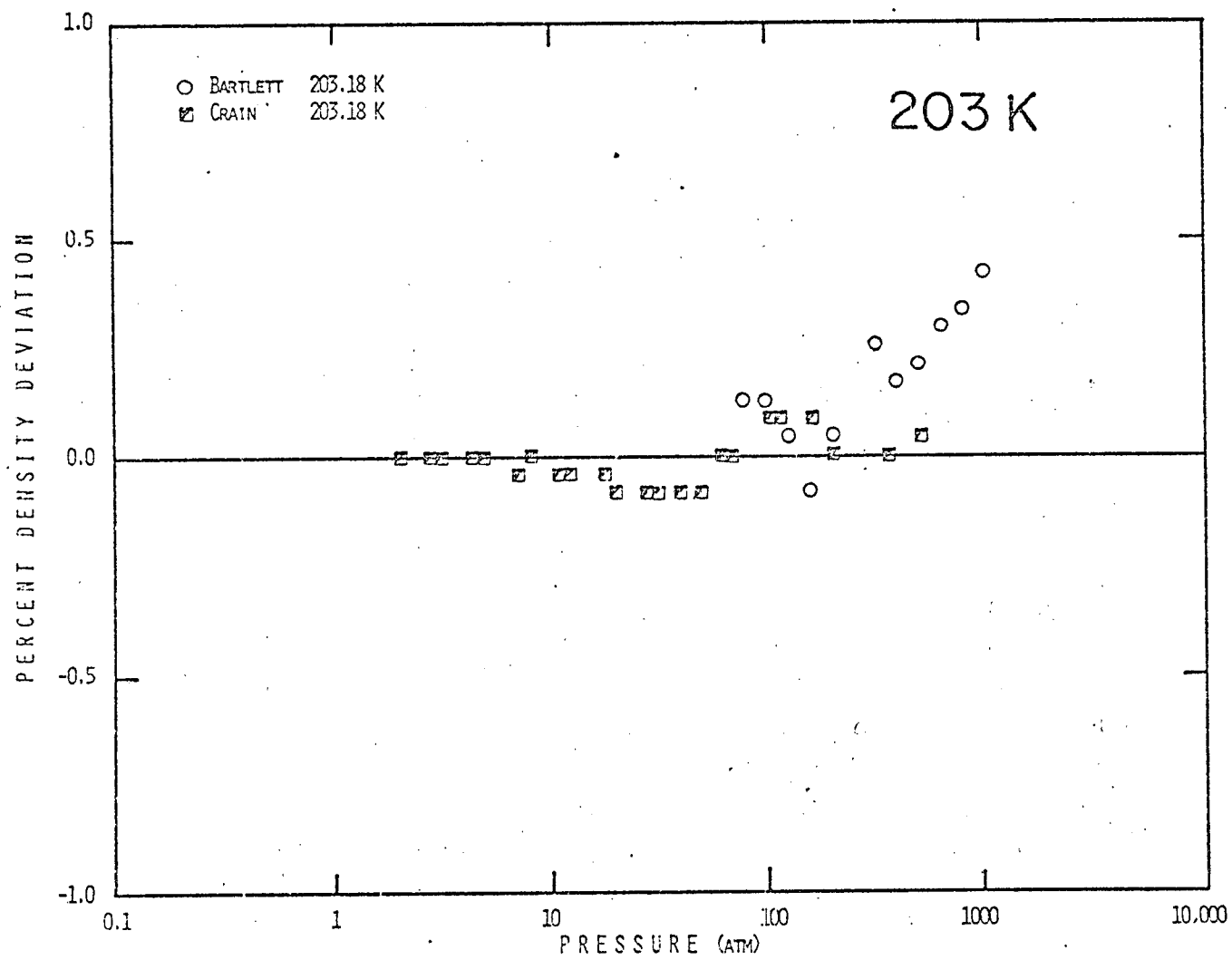   Experimental Data of [N-6, N-9].

Figure 9   Deviations in Density of Equation (2) from the
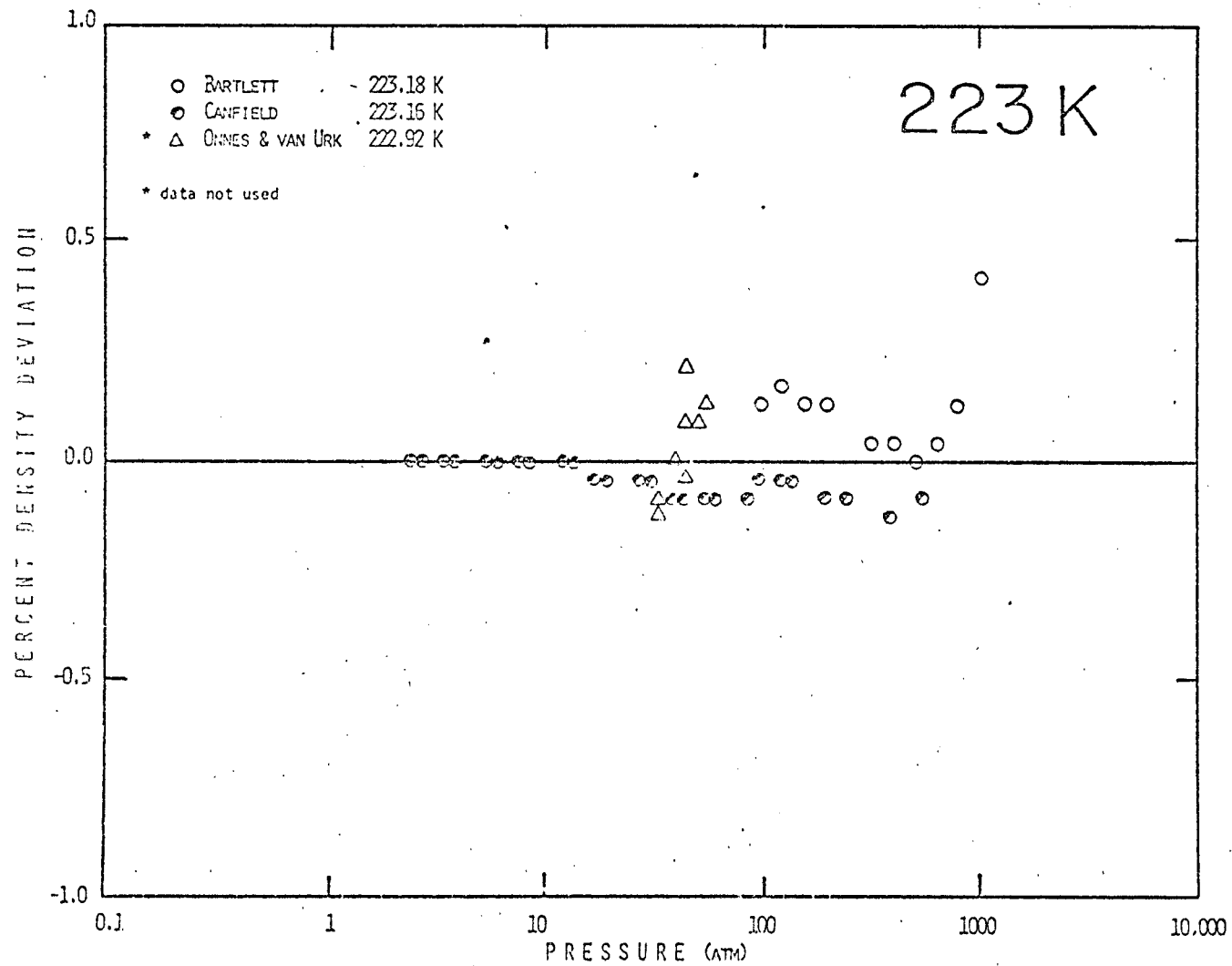Experimental Data of [N-4, N-8].

Figure 10 Deviations in Density of Equation (2) from
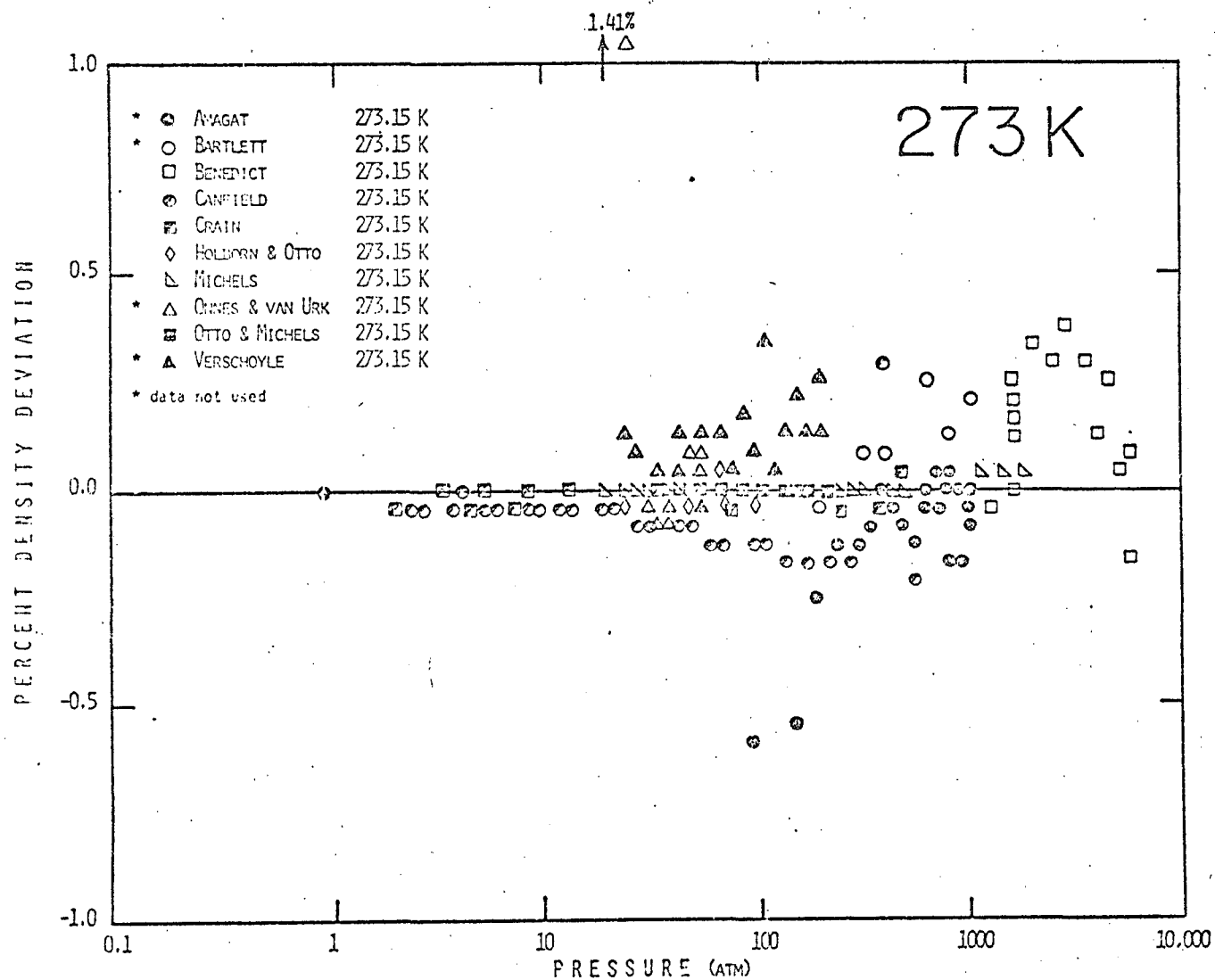the Experimental Data of [N-4, N-7, N-18].

.1.41%

1.0

273 K

*	◉	Amagat	273.15 K	
*	○	Bartlett	273.15 K	
	□	Benedict	273.15 K	
	◉	Canfield	273.15 K	
	▣	Crain	273.15 K	
	◇	Holborn & Otto	273.15 K	
	◺	Michels	273.15 K	
*	△	Onnes & van Urk	273.15 K	
	▣	Otto & Michels	273.15 K	
*	▲	Verschoyle	273.15 K	

* data not used

PERCENT DENSITY DEVIATION

0.5

0.0

-0.5

-1.0

0.1   1   10   100   1000   10,000

PRESSURE (ATM)

Figure 11   Deviations in Density of Equation (2) from
the Experimental Data of [N-1, N-3, N-6,
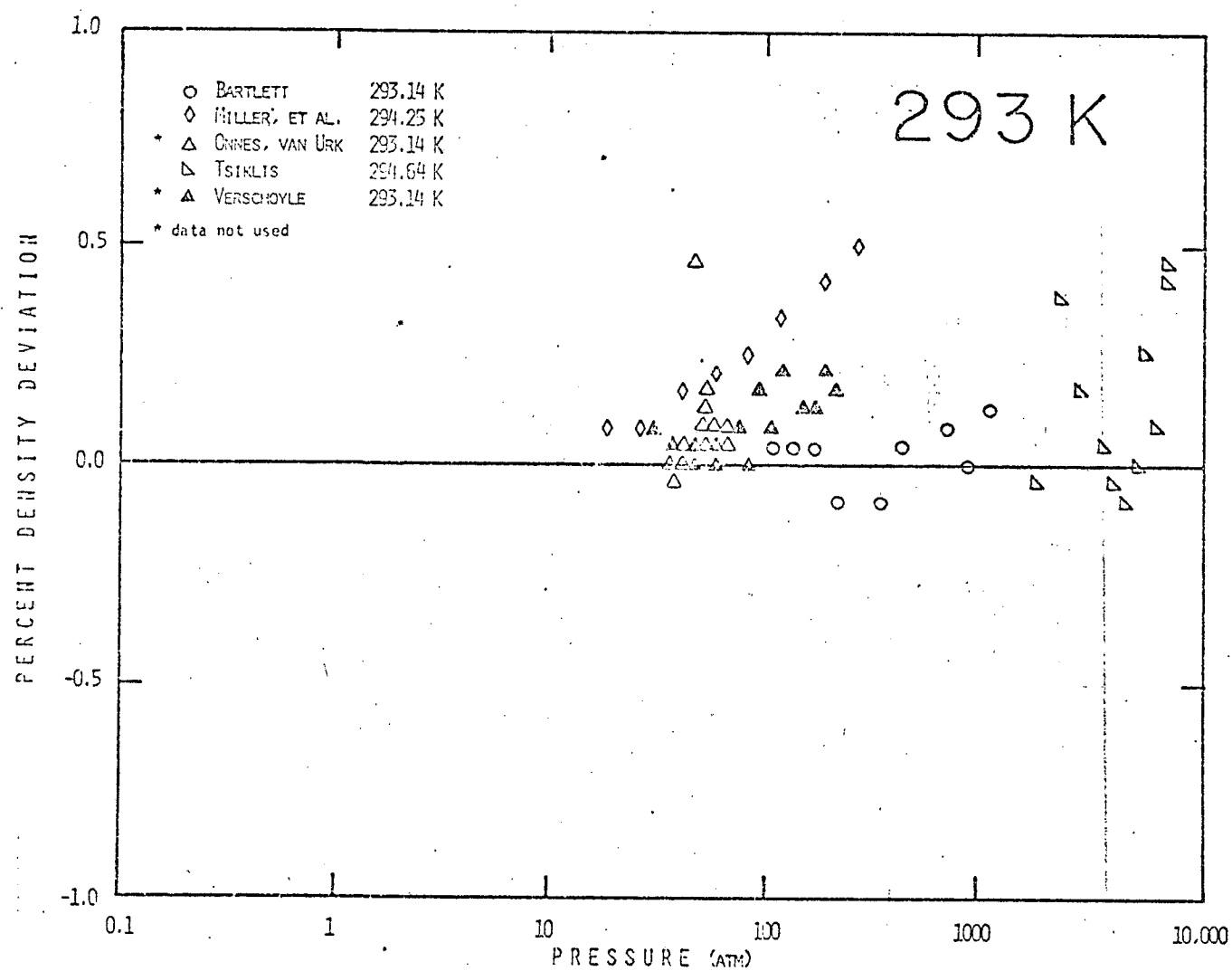N-7, N-8, N-16, N-17, N-21, N-22, N-18,
N-24, N-34].

Figure 12 Deviations in Density of Equation (2) from the
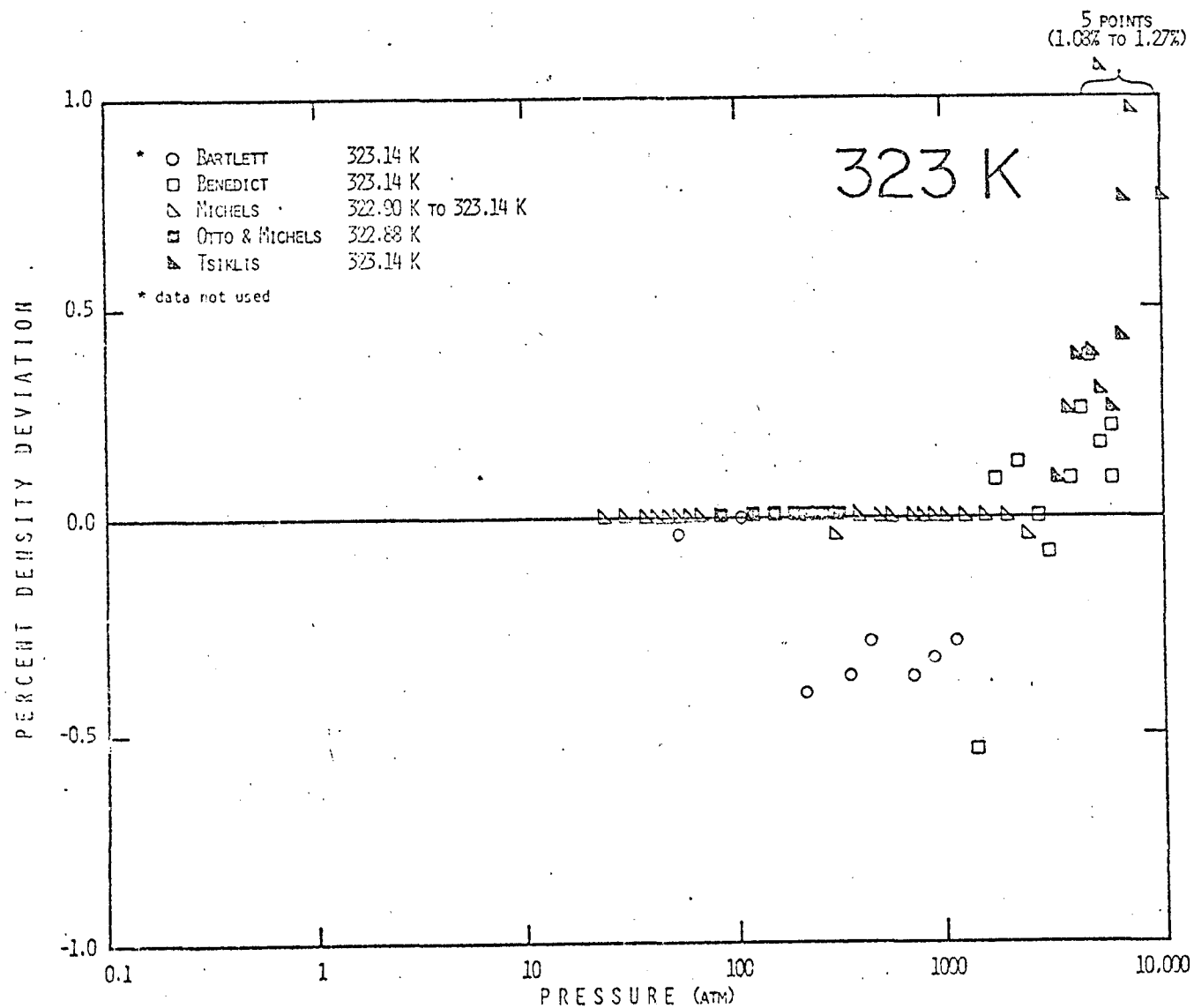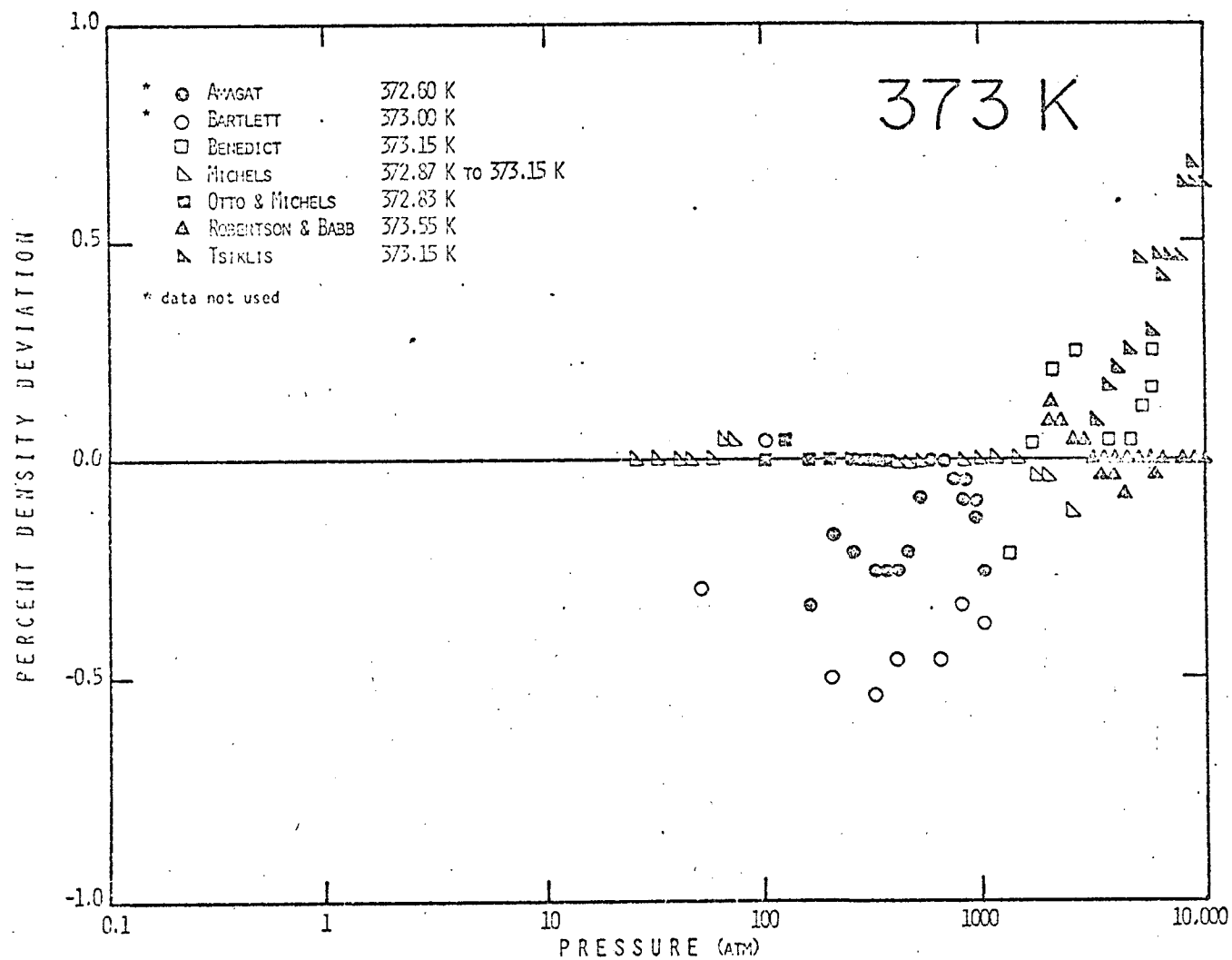Experimental Data of [N-3, N-23, N-18, N-30, N-34].

1.0

```
   *  O  BARTLETT        323.14 K
      □  BENEDICT        323.14 K
      △  MICHELS         322.90 K to 323.14 K
      ▱  OTTO & MICHELS  322.88 K
      ◣  TSIKLIS         323.14 K

   * data not used
```

323 K

PERCENT DENSITY DEVIATION

0.5

0.0

-0.5

-1.0

0.1   1   10   100   1000   10,000

PRESSURE (ATM)

Figure 13   Deviations in Density of Equation (2) from the
            Experimental Data of [N-3, N-6, N-21, N-22,
            N-24, N-31].

Figure 14 Deviations in Density of Equation (2) from the
Experimental Data of [N-1, N-3, N-6, N-21,
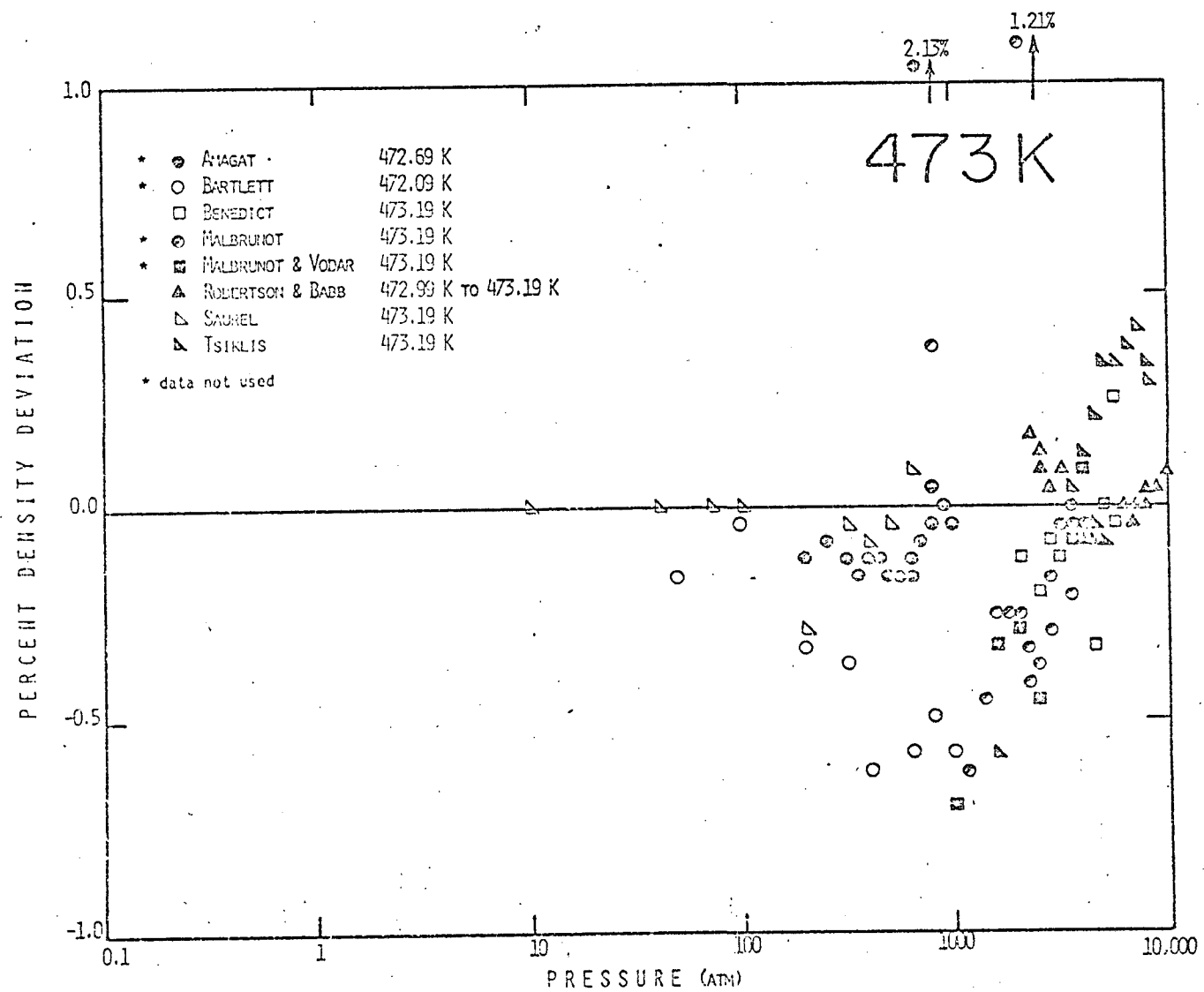N-22, N-24, N-25, N-31].

Figure 15   Deviations in Density of Equation (2) from the
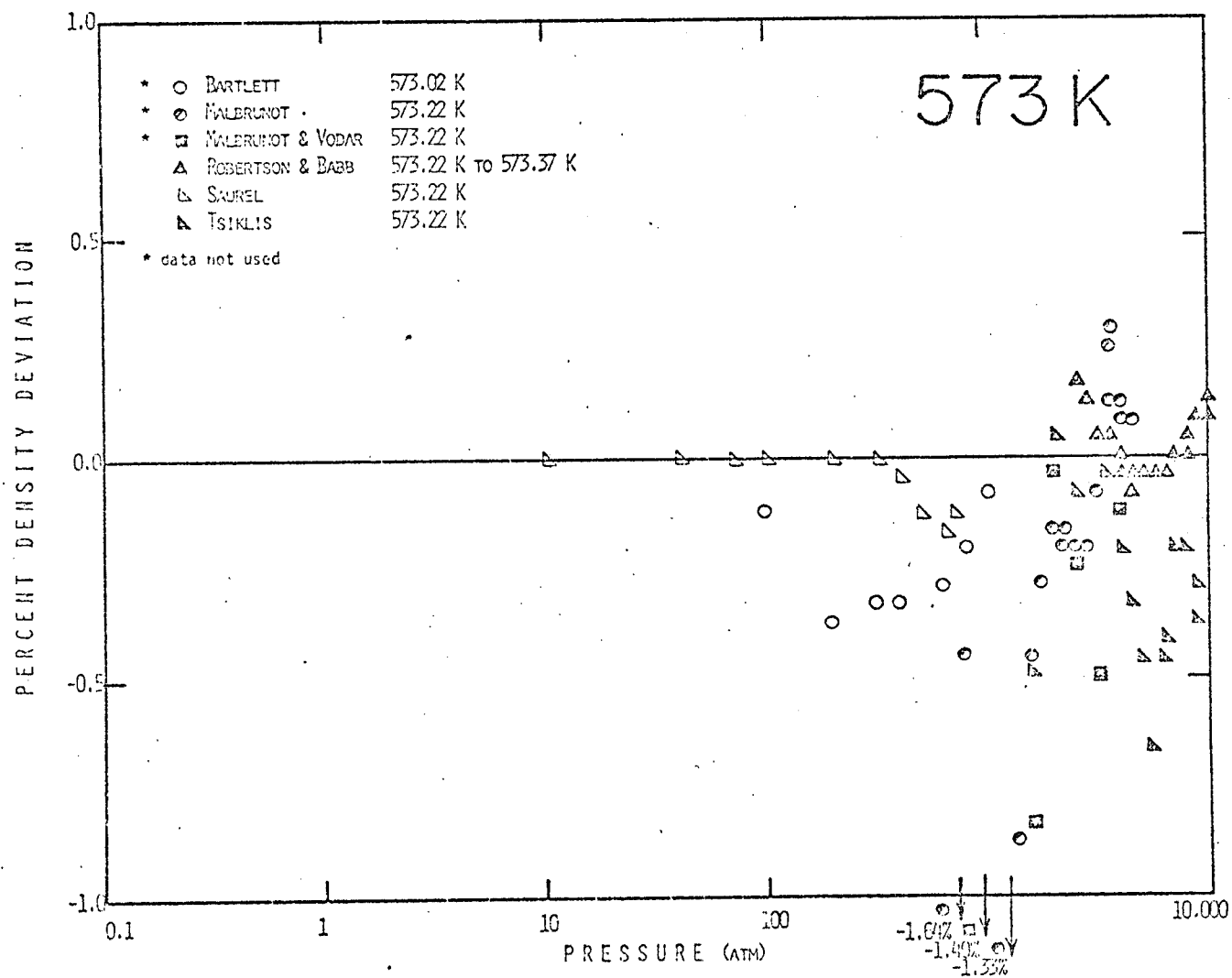Experimental Data of [N-1, N-3, N-6, N-20, N-19
N-25, N-26, N-30].

Figure 16 Deviations in Density of Equation (2) from the
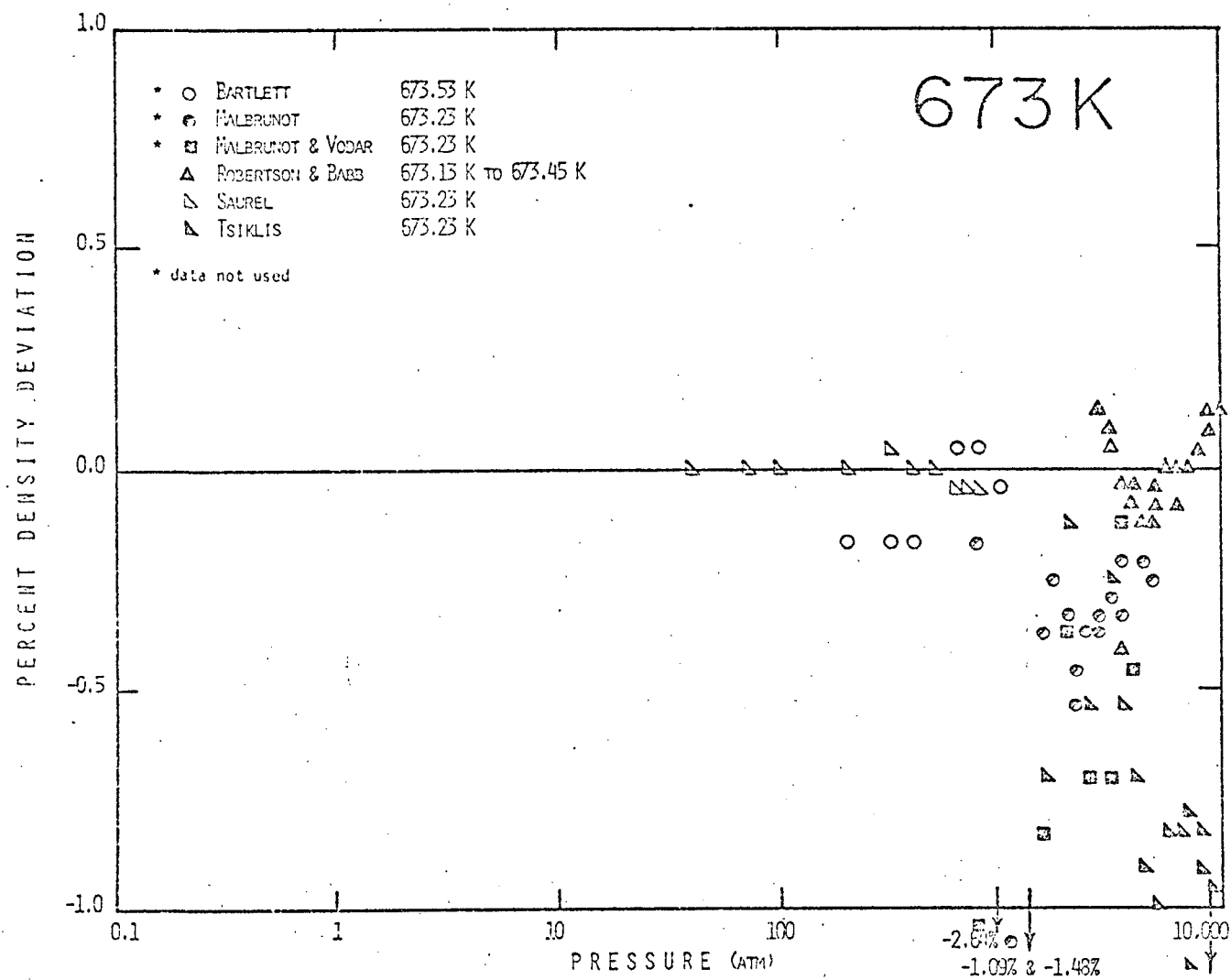Experimental Data of [N-3, N-20, N-19, N-25, N-26,
N-30].

1.0

673 K

		BARTLETT	673.53 K
*	O	BARTLETT	673.53 K
*	e	MALBRUNOT	673.23 K
*	▣	MALBRUNOT & VODAR	673.23 K
	△	ROBERTSON & BABB	673.13 K TO 673.45 K
	◺	SAUREL	673.23 K
	◮	TSIKLIS	673.23 K

* data not used

PERCENT DENSITY DEVIATION

0.5

0.0

-0.5

-1.0

0.1   1   10   100   10,000

PRESSURE (ATM)

-2.6%

-1.09% & -1.46%

3 POINTS
(-1.07% TO -1.52%)

Figure 17   Deviations in Density of Equation (2) from the
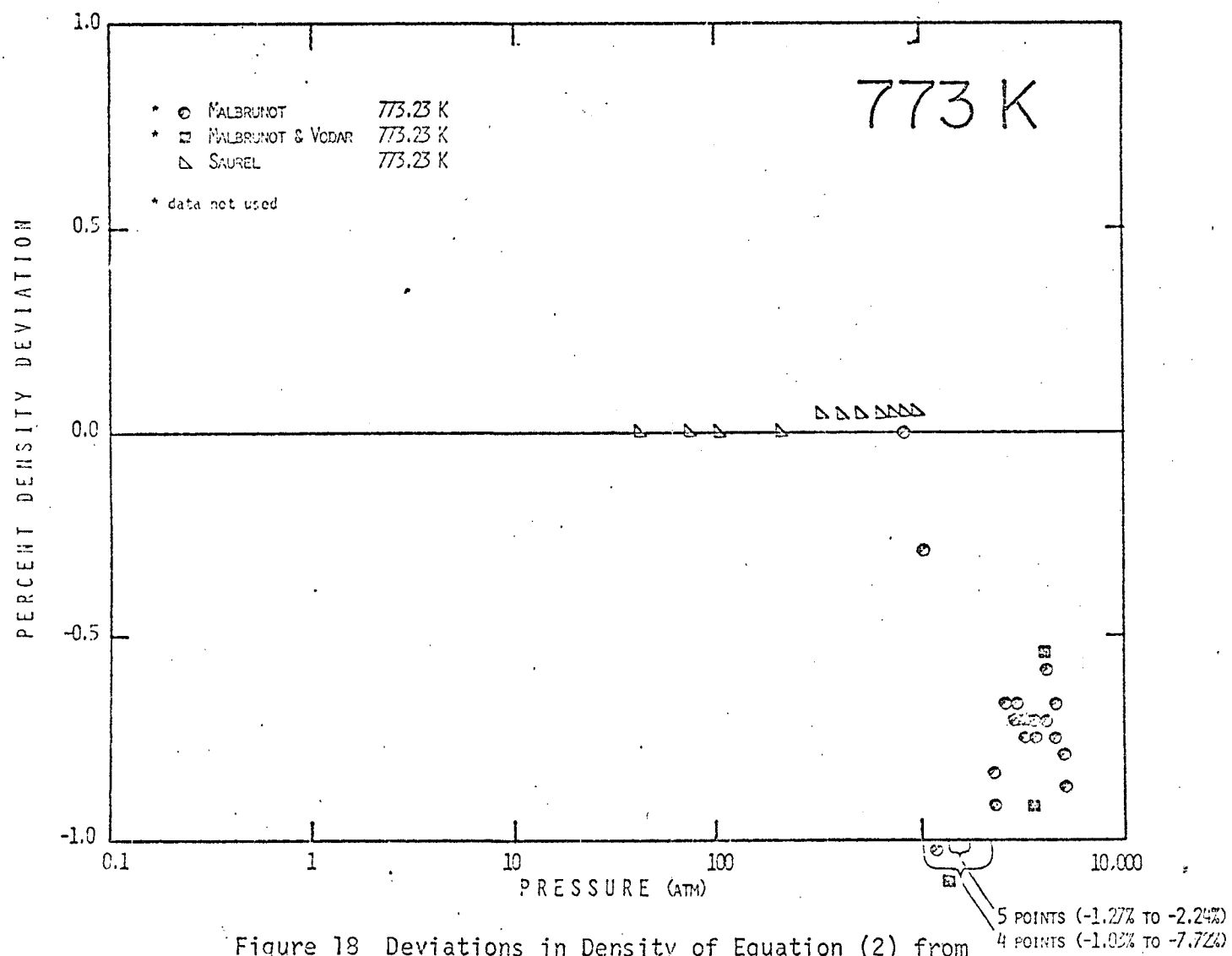Experimental Data of [N-3, N-20, N-19, N-25,
N-26, N-30].

Figure 18 Deviations in Density of Equation (2) from
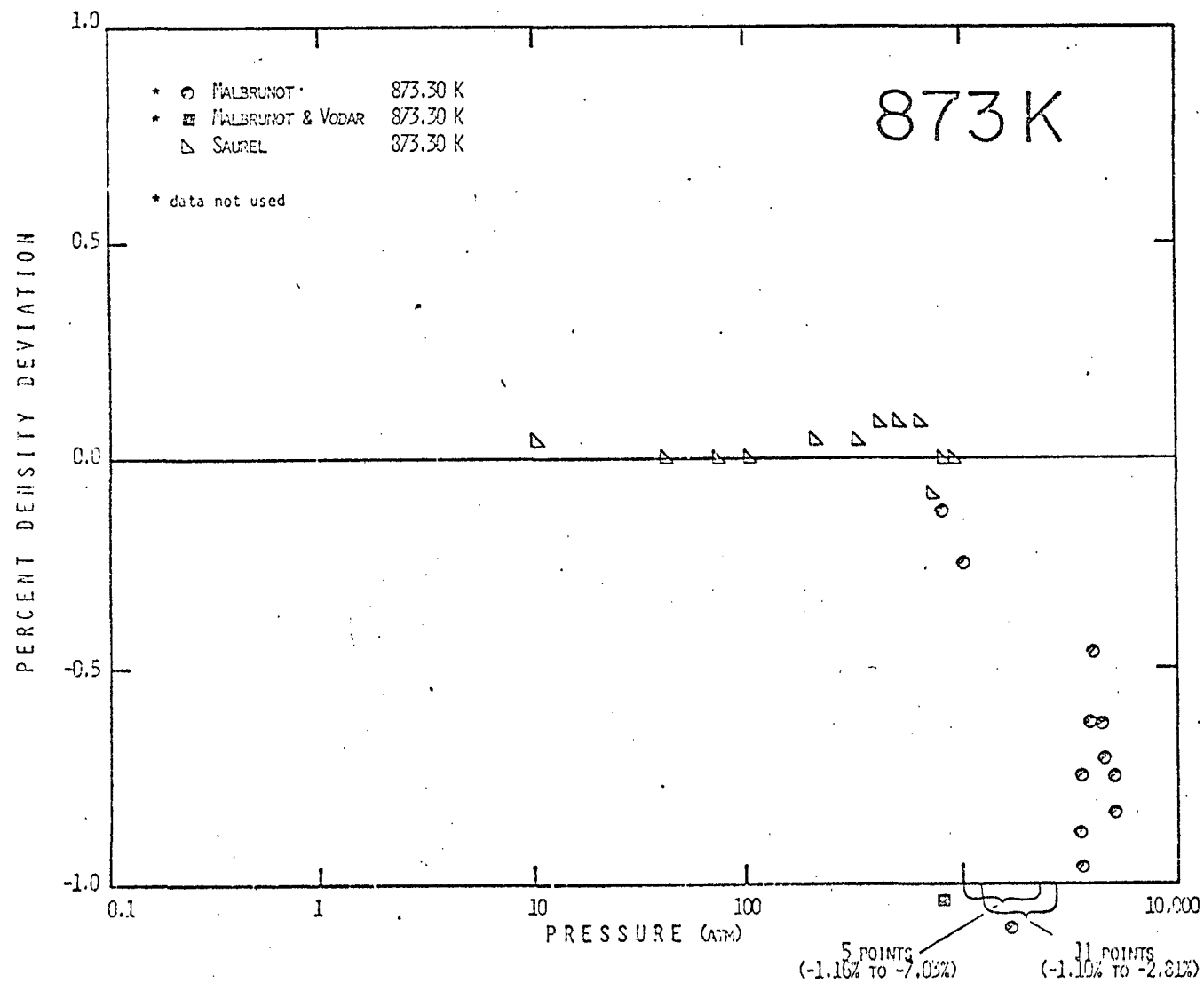the Experimental Data of [N-20, N-19, N-26].

Figure 19   Deviations in Density of Equation (2) from the
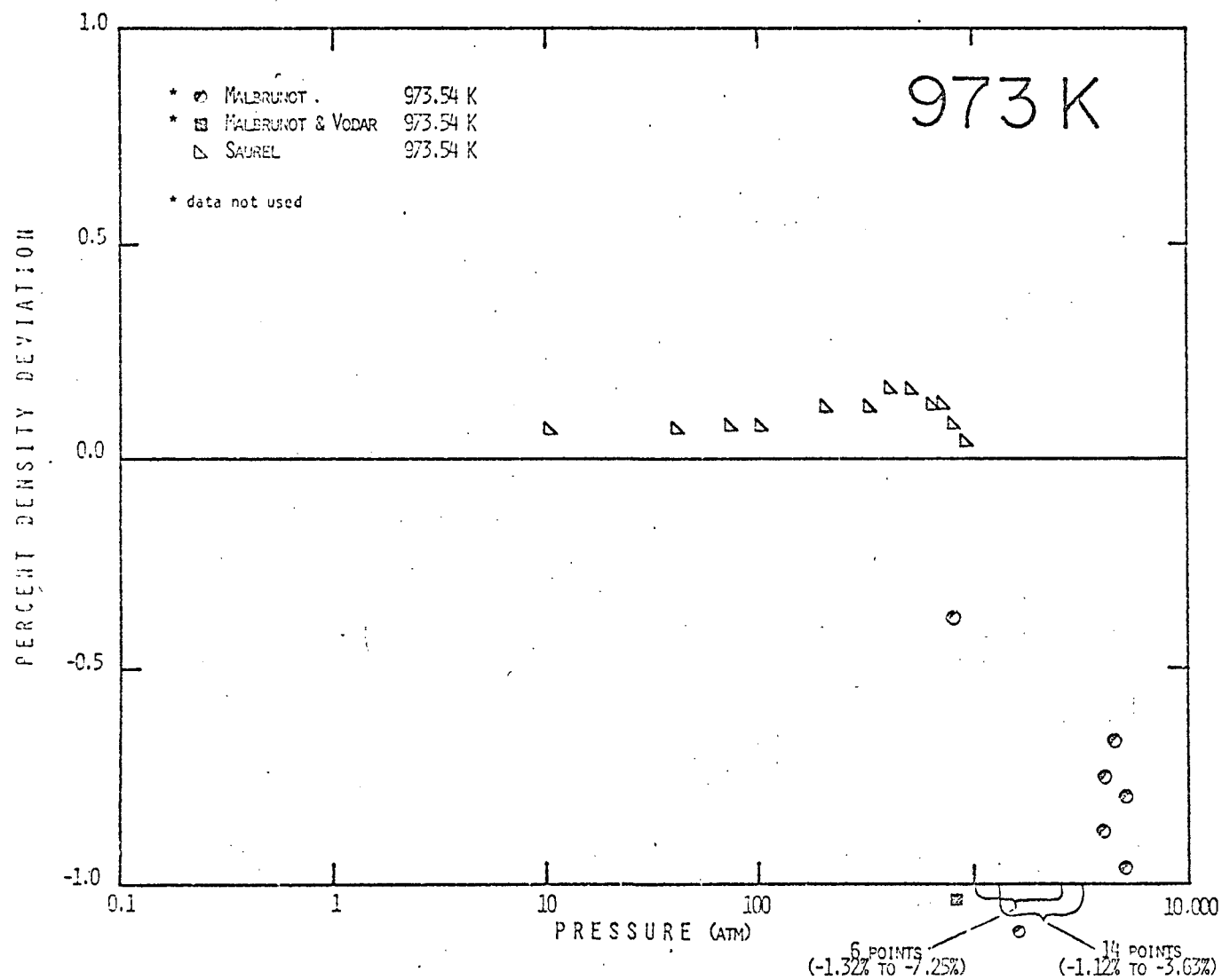Experimental Data of [N-20, N-19, N-26].

Figure 20 Deviations in Density of Equation (2) from the
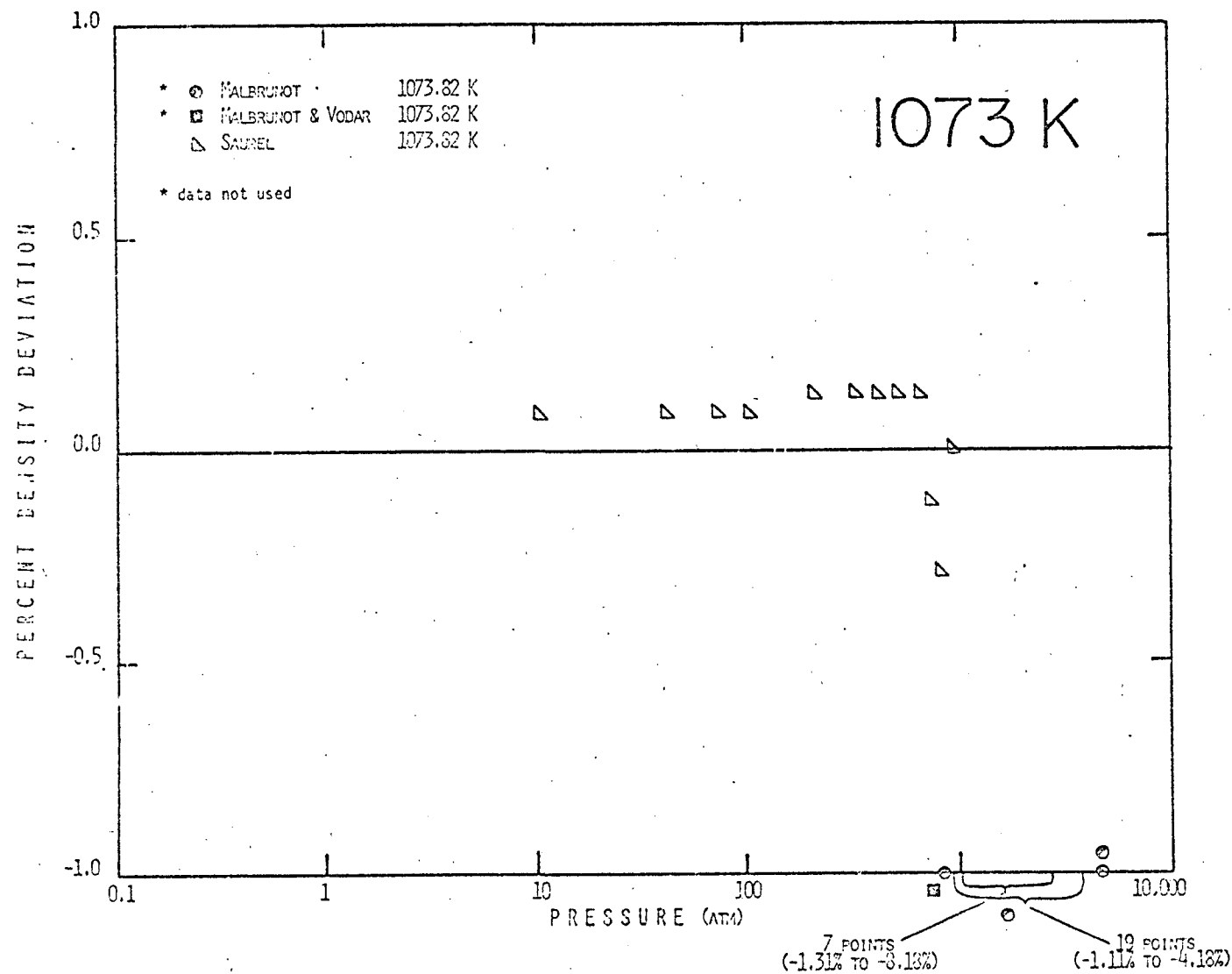Experimental Data of [N-20, N-19, N-26].

30.

Figure 21   Deviations in Density of Equation (2) from the
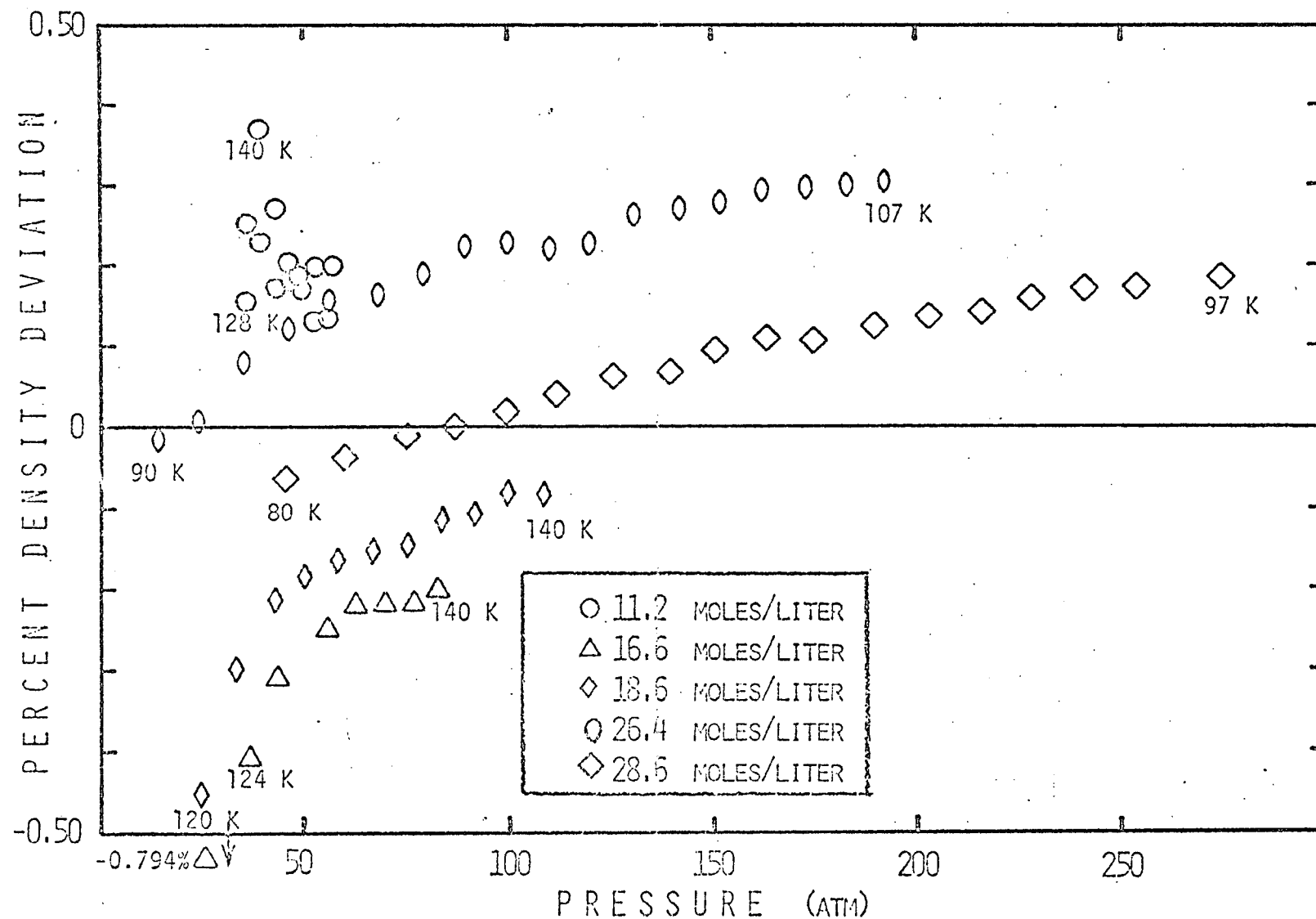Experimental Data of [N-20, N-19, N-26].

Figure 22 Density Deviations of Equation (2) from Isochoric Data of Weber [N-35]
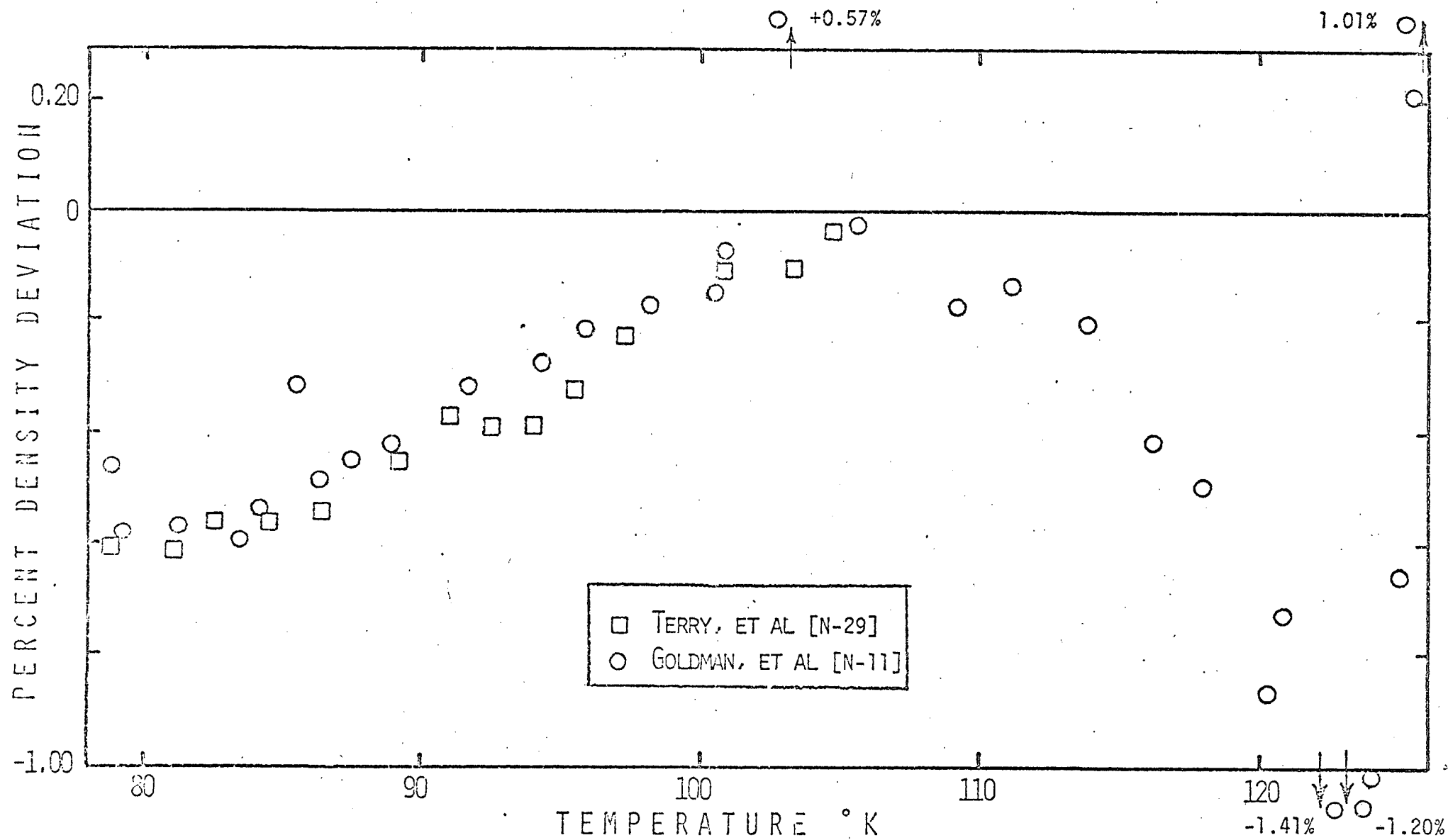(The minimum and maximum temperatures for each isochor are noted.)

Figure 23   Deviations of Equation of State from Liquid P-ρ-T Data at the Vapor Pressure
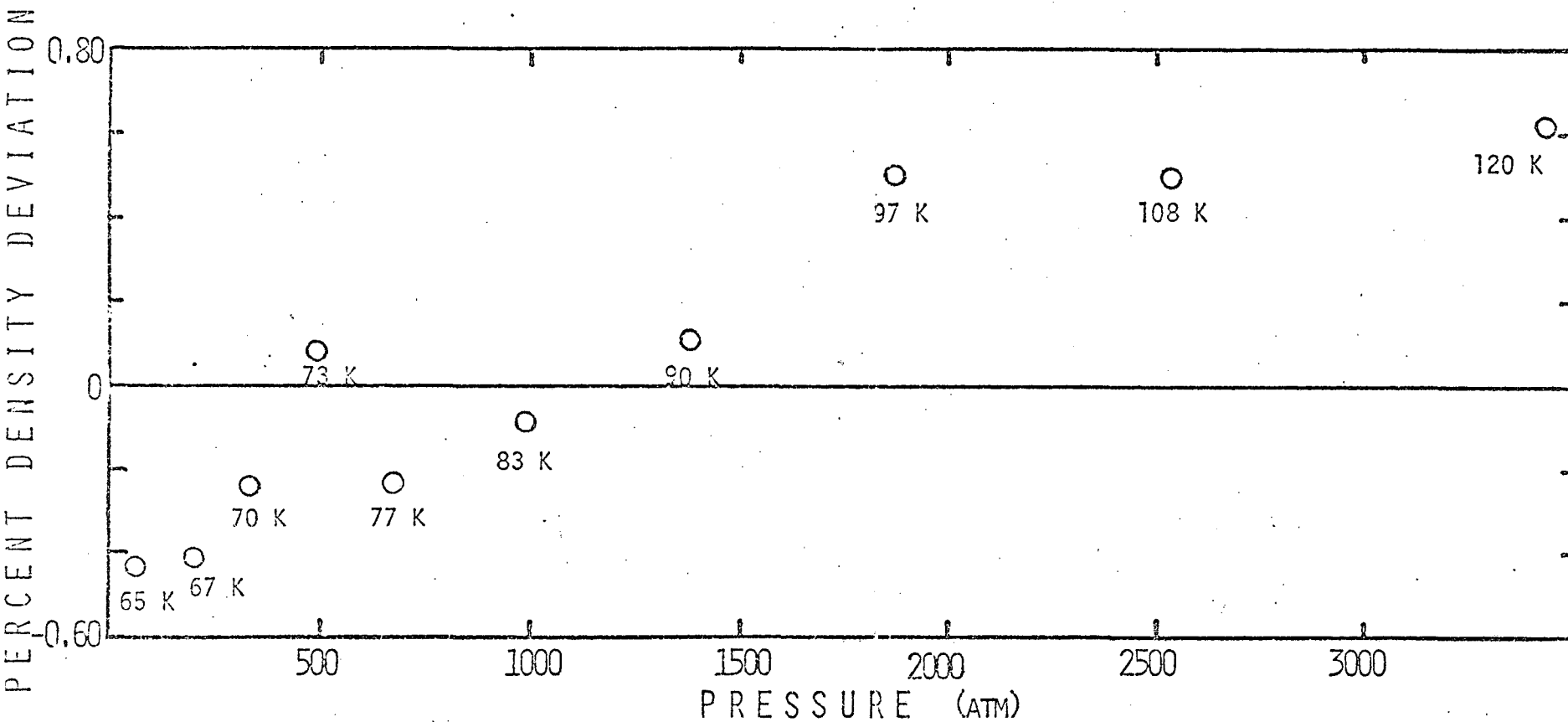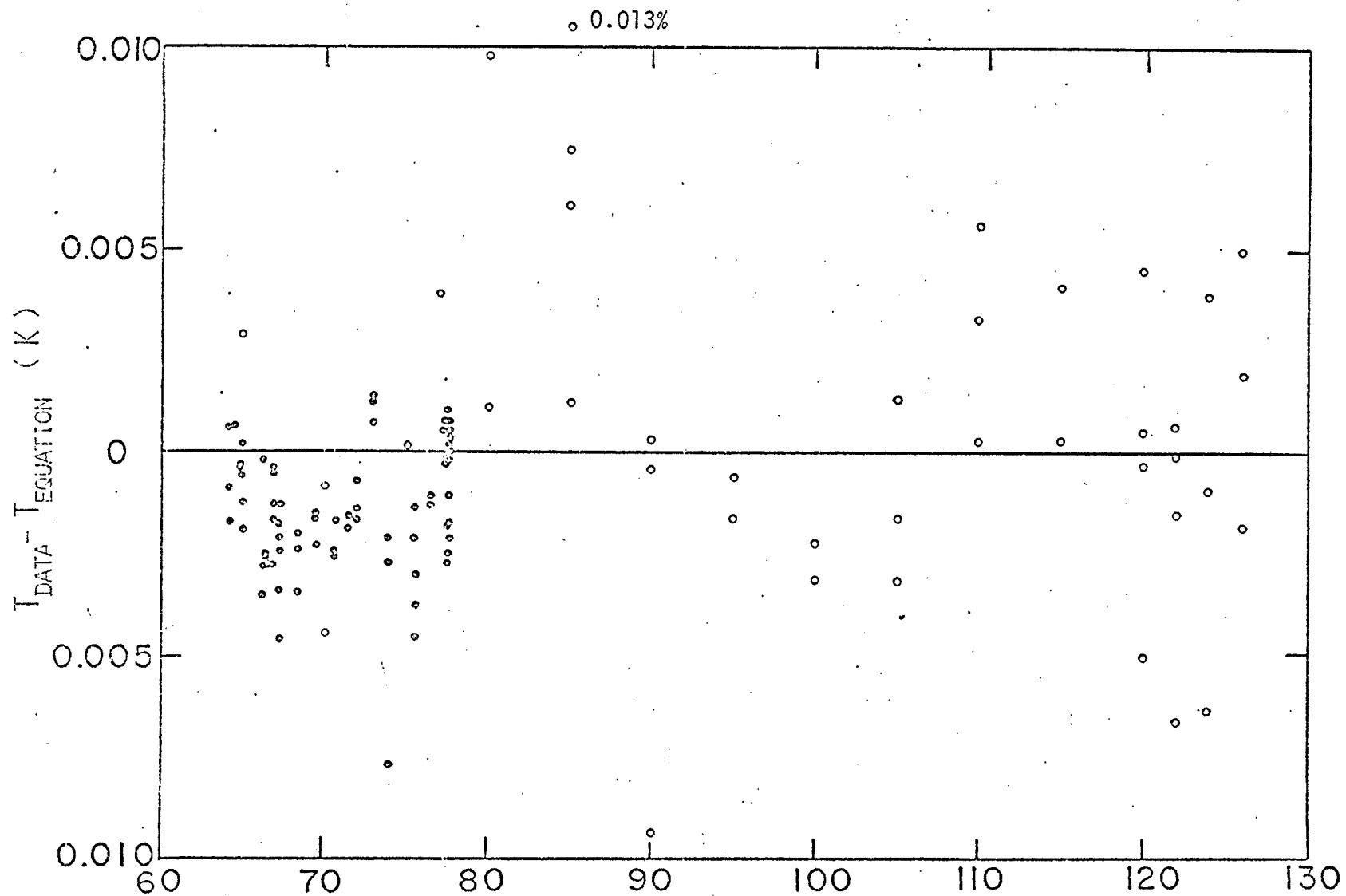
Figure 24   Deviations of Equation (2) from Liquid P-ρ-T Data on the Freezing Line
(Nominal temperatures are given below each point), from [N-13].

Figure 25 Deviations of Nitrogen Vapor Pressure Equation from Selected Vapor Pressure Data.

III WORK ACCOMPLISHED DURING QUARTER ENDING OCTOBER 1, 1971

A.   Thermodynamic Properties of Oxygen

A review of [1] and of the thermodynamic property literature published sub-
sequently, indicate that the data of Weber [0-1], Michels, Schamp, and DeGraaff
[0-2], and Nijhoff and Keesom [0-3], are adequate to describe the P-ρ-T surface
for the range of pressure and temperature for which P-ρ-T measurements have been
published. Other measurements of P-ρ-T data are all within the ranges covered
by these selected data, and are considered less accurate. The equation of state
previously developed for nitrogen [equation (2)] has, therefore, been fit to the
data of [0-1, 0-2, 0-3]. The resulting coefficients are given in Table VI for
temperatures in degrees Kelvin, pressures in atmospheres, and density in moles/
liter.

Figures 26 to 48 illustrate the deviations between measurements of density
and density values calculated by the equation of state (2), (i.e., the percent
density deviation, $[(\rho_{exp} - \rho_{calc})/\rho_{exp}] \times 100$, where ρ_{exp} represents the observed
density reported by the experimenter, and ρ_{calc} the density calculated from equa-
tion (2) for each experimental pressure and temperature). The temperature for
which these comparisons are given were selected to present a representative
analysis of the available data, and to cover the range of temperatures for which
data are available. The following comments are made with regard to the compari-
son in figures 26 to 48.

The data for the liquid are illustrated in figures 26 to 37 for tempera-
tures from 65 K to 150 K. The data of Van Itterbeek and Verbeke [0-4] from 65 K
to 90 K illustrate many of the same characteristics exhibited by their data for
nitrogen, (i.e., the data deviate systematically from other data). However, in
the case of oxygen, their values at 85 K and 90 K are concordant with the data
published by Weber [0-1].

It is notable that the density deviations for the liquid illustrated here
indicate the data of [0-1] to be more precise than similar deviation illustra-
tions published in [1]. Much of the increased precision in the liquid data may
be attributed to corrections applied to the oxygen measurements made by Weber
subsequent to their earlier use in determining the equation of state reported in
[1].

Table VI

Coefficients for the Equation of State (2) for Oxygen

N_1 = 0.655793661 N_{19} = $-0.8551604876 \times 10^6$

N_2 = $-0.5002477226 \times 10^2$ N_{20} = $-0.6014514417 \times 10^7$

N_3 = 0.1504934668×10^4 N_{21} = 0.5447328659×10^2

N_4 = $-0.2179011942 \times 10^5$ N_{22} = $-0.1268996671 \times 10^5$

N_5 = 0.1367195269×10^6 N_{23} = 0.8519690420×10^6

N_6 = $-0.3219399039 \times 10^7$ N_{24} = 0.1624562257

N_7 = 0.6973943732×10^8 N_{25} = $-0.4132191472 \times 10^2$

N_8 = $-0.8167967424 \times 10^9$ N_{26} = 0.3049444743×10^4

N_9 = $0.2504317191 \times 10^{-5}$ N_{27} = $-0.2947724877 \times 10^{-4}$

N_{10} = $-0.1629586798 \times 10^{-2}$ N_{28} = $0.4353294667 \times 10^{-1}$

N_{11} = 0.4495749573 N_{29} = $-0.6027003795 \times -0^1$

N_{12} = $-0.7785655532 \times 10^2$ N_{30} = $0.1417839254 \times 10^{-6}$

N_{13} = 0.4758631651×10^4 N_{31} = $-0.5512870869 \times 10^{-4}$

N_{14} = $-0.7499817414 \times 10^{-5}$ N_{32} = $0.6224757338 \times 10^{-2}$

N_{15} = $0.1567080218 \times 10^{-2}$ N_{33} = $0.1444591074 \times 10^{-9}$

N_{16} = $0.1415624001 \times 10^{-3}$ N_{34} = $-0.1422601846 \times 10^{-7}$

N_{17} = $-0.1279461017 \times 10^{-1}$ N_{35} = $-0.9115572086 \times 10^{-6}$
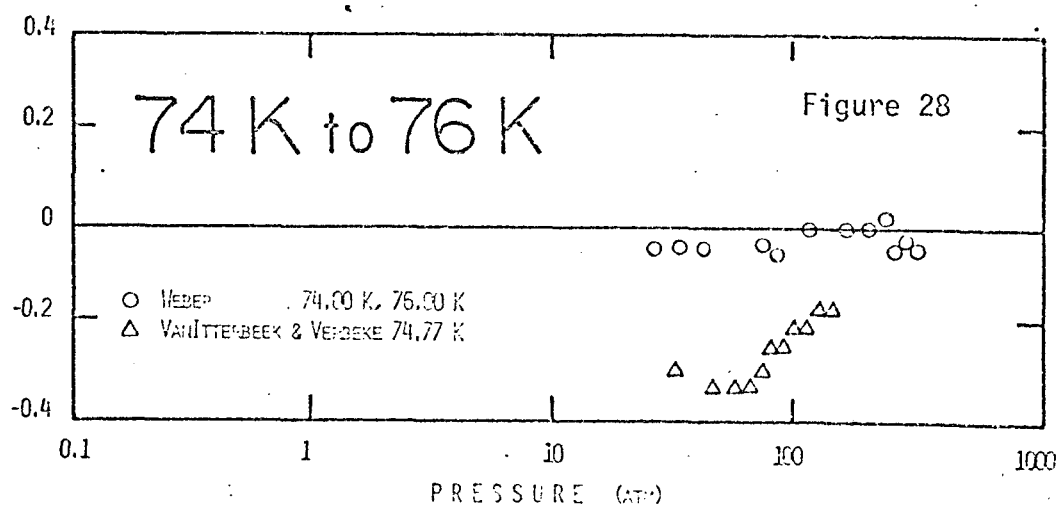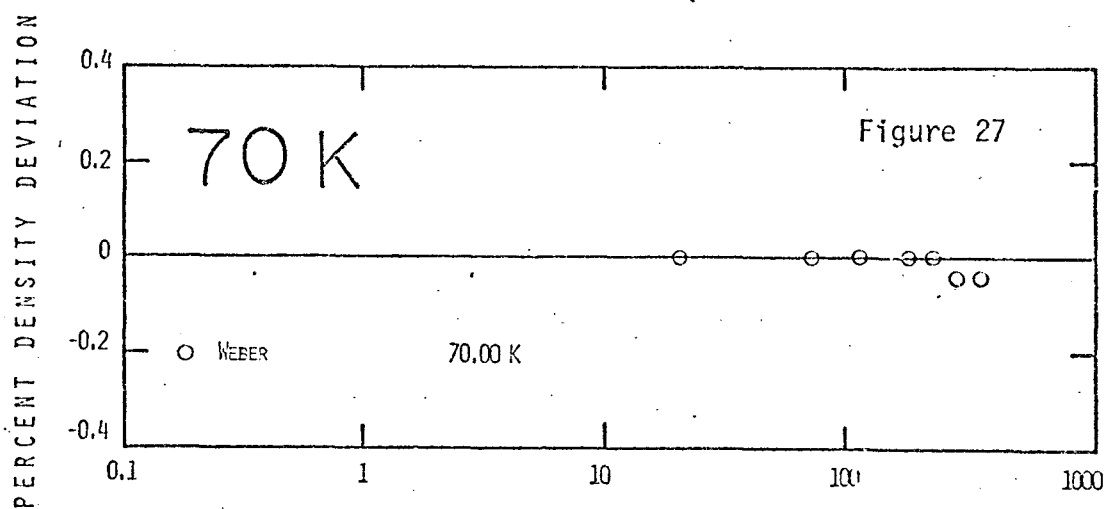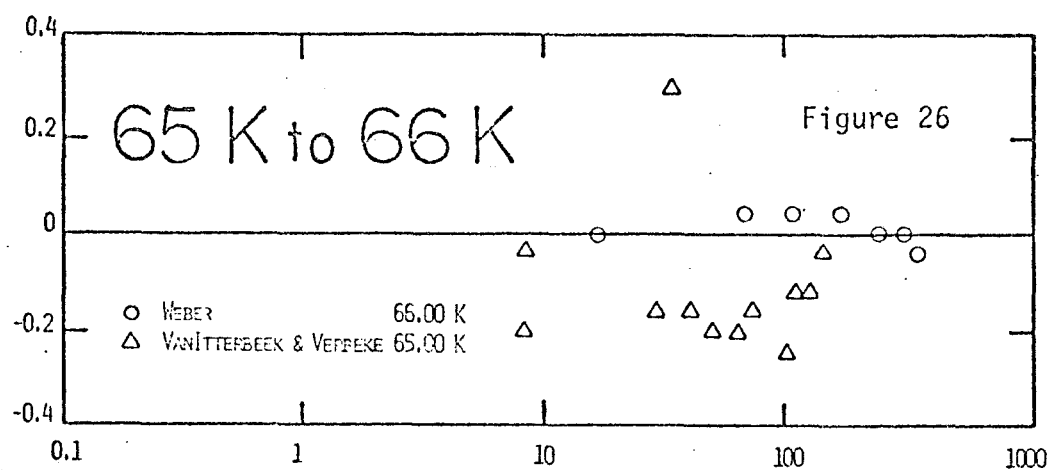
N_{18} = 0.7559211303×10^4
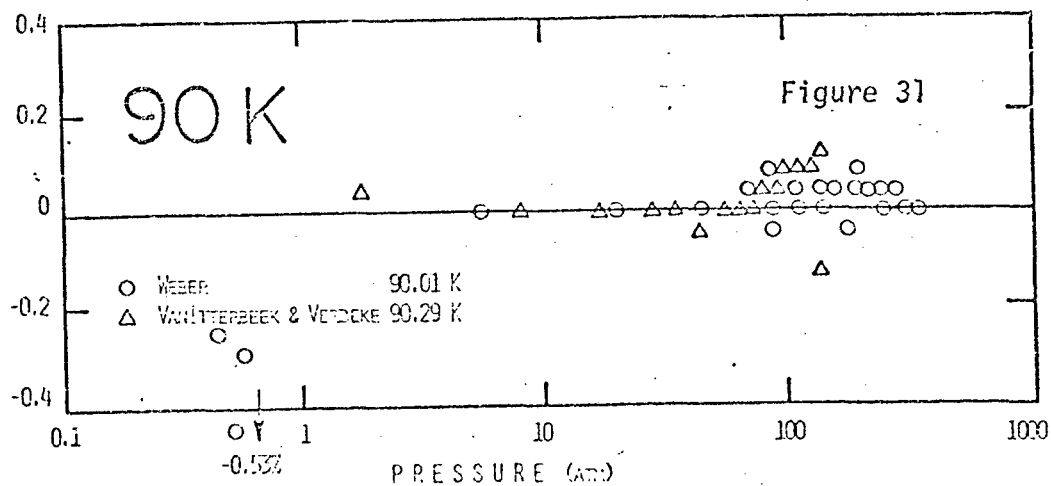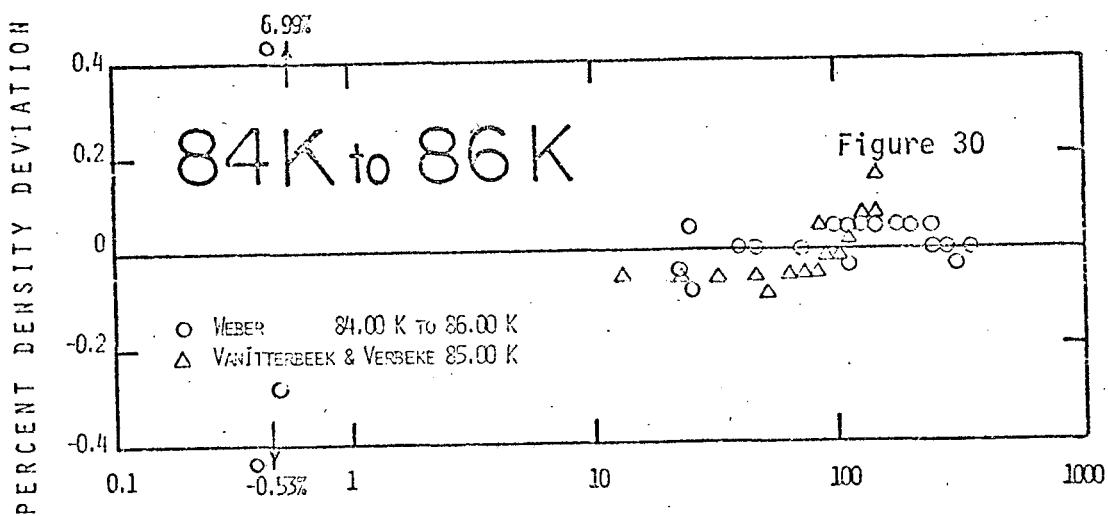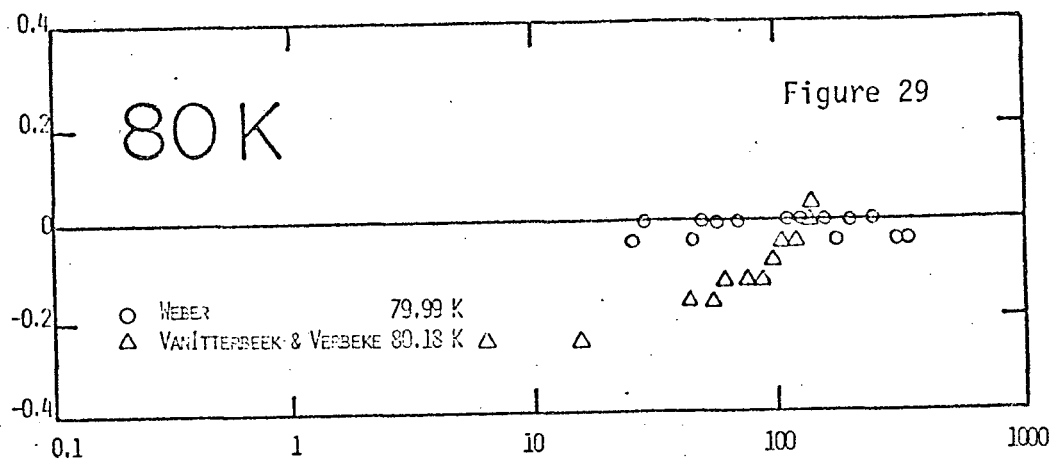
γ = 0.0056

R = 0.0820535 liter-atm/mol-K

Comparisons of densities calculated from equation (2) with P-ρ-T data for the low temperature-low pressure vapor are included in figures 32 to 44 for temperatures from 99 K to 233 K. (These figures also include comparisons to liquid data for pressures over 10 atm. which are discussed above.) The low pressure vapor measurements by Weber [O-1] for temperatures from 99 K to 140 K are of lower precision than the measurements made by Weber for higher densities. The equation represents the older data of Nijhoff and Keesom [O-3] with approximately the same accuracy as the earlier equation of state in [1].

The equation of state is not as accurate for the higher density values from 170 K to 300 K as the earlier equation in [1], as indicated by comparisons with Weber's data. The systematic deviations between the equation and the data is a consequence of the fitting problems near the critical point. This same problem was present for the nitrogen equation reported in [7]. This is not a new problem, since these same systematic deviations are also noted in the deviation graphs in [1]. The equation of state reported here fits the higher temperature data by Michels et al. [O-2] better than the earlier equation in [1].
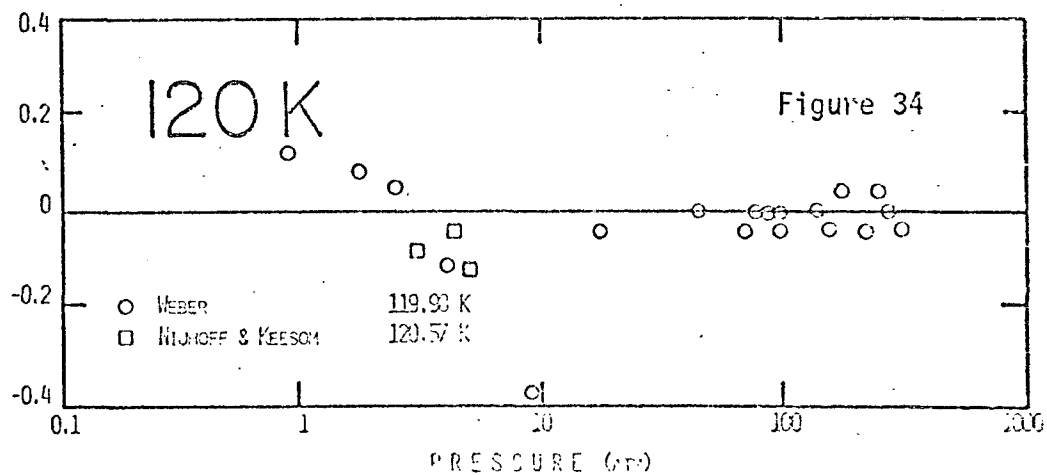
Values of heat capacity calculated using this equation exhibit erratic behavior in the liquid range, and deviate significantly from measured values reported in [O-1] near the critical temperature. (Further study of the equation of state for oxygen employing simultaneous fitting of heat capacity values and P-ρ-T data will be made to eliminate these problems.)

Figure 26

65 K to 66 K

○ Weber 66.00 K
△ VanItterbeek & Verbeke 65.00 K

Figure 27

70 K

○ Weber 70.00 K

Figure 28

74 K to 76 K

○ Weber 74.00 K, 76.00 K
△ VanItterbeek & Verbeke 74.77 K

PERCENT DENSITY DEVIATION

PRESSURE (atm)

Deviations in Density of Equation (2) from the Experimental data of [0-1, 0-4].

Deviations in Density of Equation (2) from the Experimental Data of [0-1, 0-4].

Deviations in Density of Equation (2) from the Experimental Data of [0-1, 0-3].

Figure 35

127 K to 130 K

○ WEBER   129.99 K
□ NIJHOFF & KEESOM   127.23 K

Figure 36

138 K to 140 K

○ WEBER   139.99 K
□ NIJHOFF & KEESOM   137.83 K

PERCENT DENSITY DEVIATION

0.515%

Figure 37

148 K to 150 K

○ WEBER   150.00 K
□ NIJHOFF & KEESOM   148.17 K

PRESSURE (atm)

Deviations in Density of Equation (2) from the Experimental Data of [O-1, O-3].

Deviations in Density of Equation (2) from the Experimental
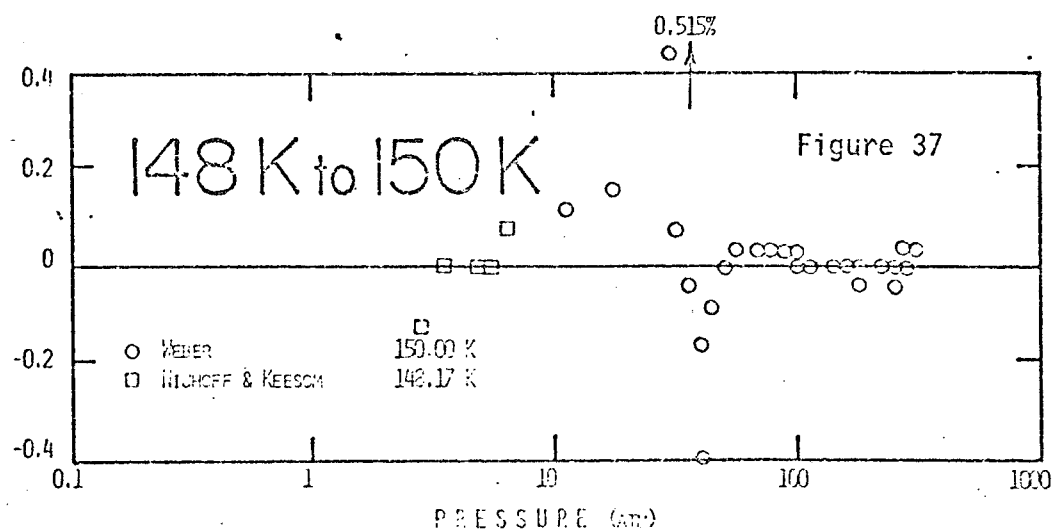Data of [O-1, O-3].

Deviations in Density of Equation (2) from the Experimental
Data of [0-1, 0-3].

Deviations in Density of Equation (2) from the Experimental Data of [0-1, 0-2, 0-3].

Figure 47 — 298 K to 300 K

O	WEBER	299.93 K
△	MICHELS	298.14 K

Figure 48 — 323 K

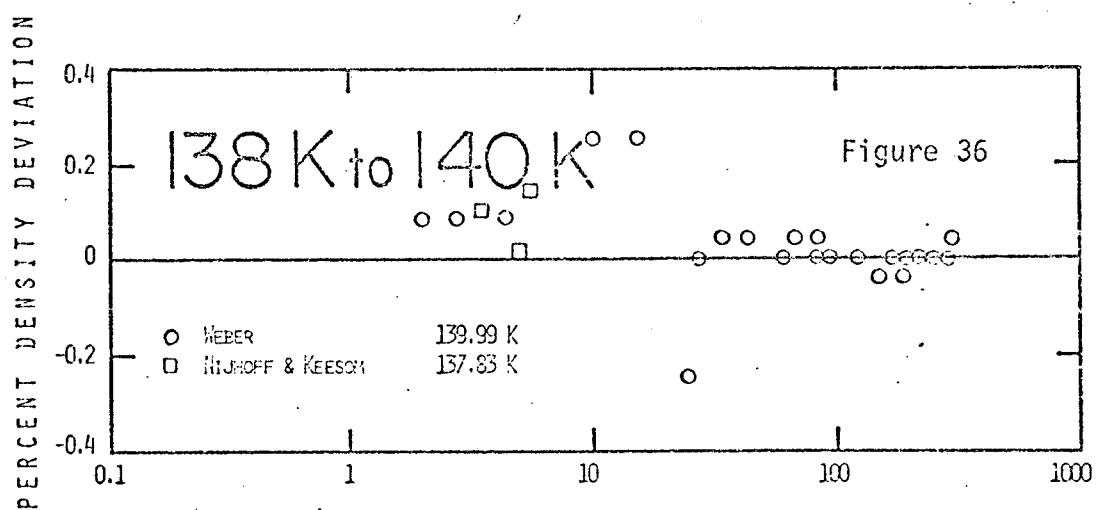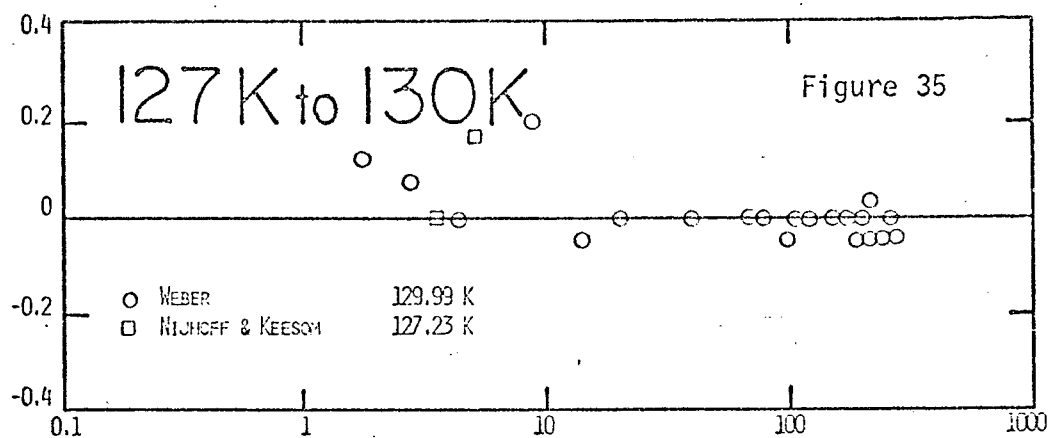|		
△	MICHELS	323.14 K

PERCENT DENSITY DEVIATION

PRESSURE (ATM)

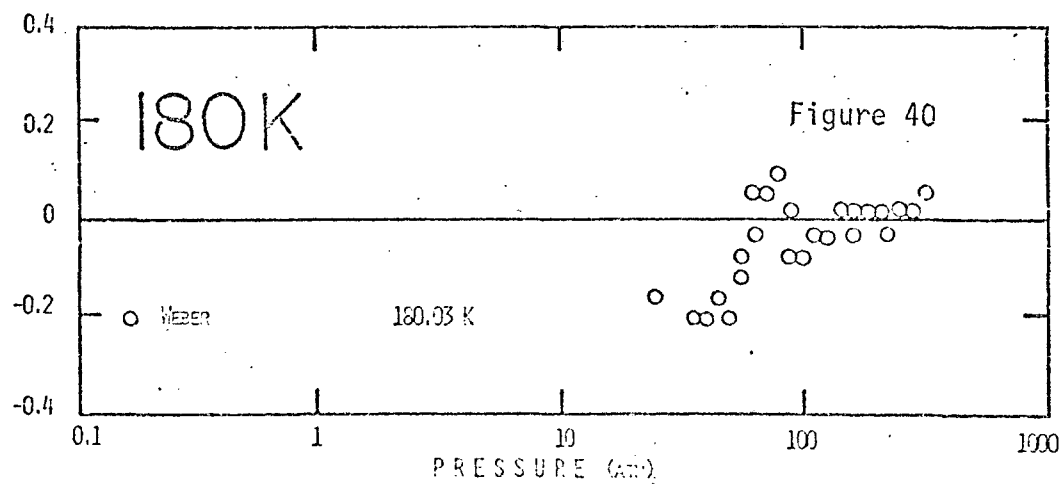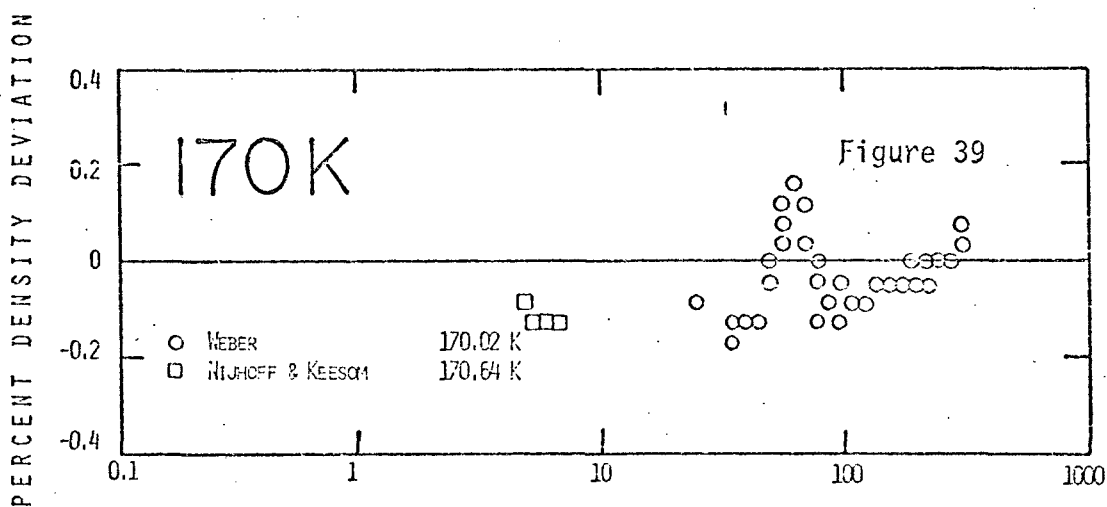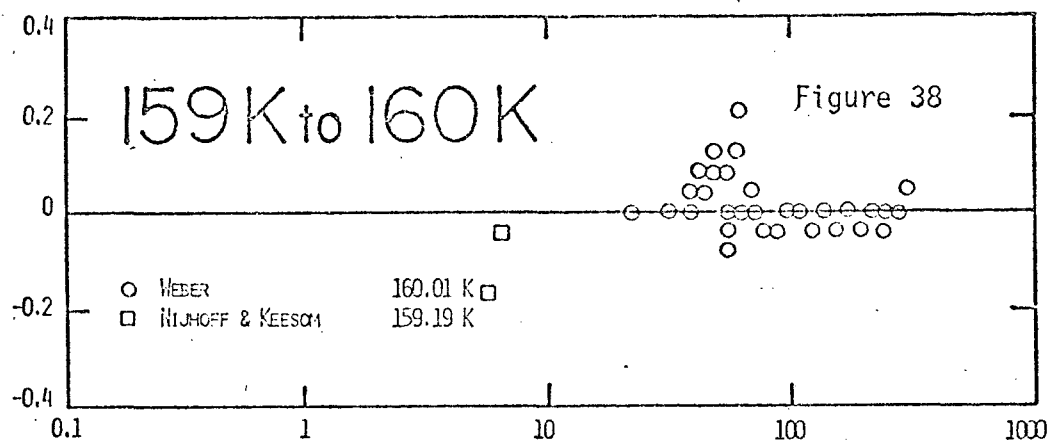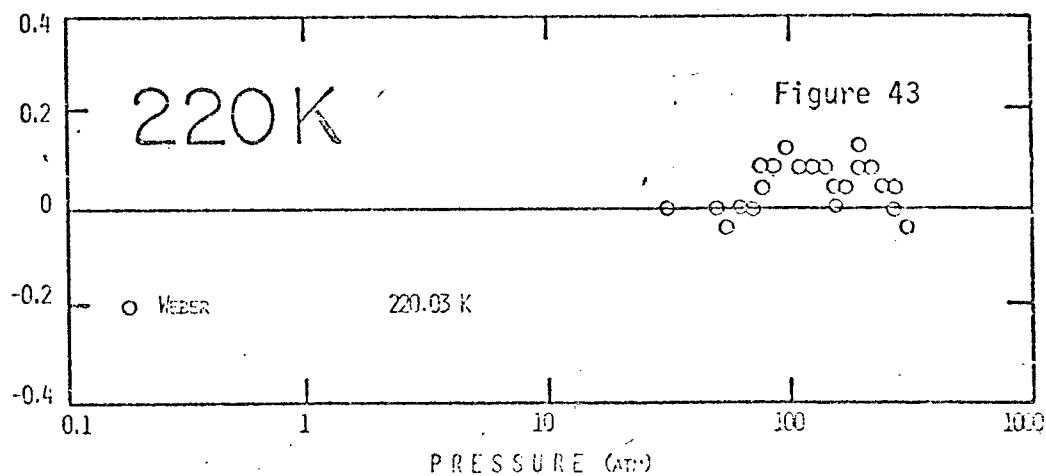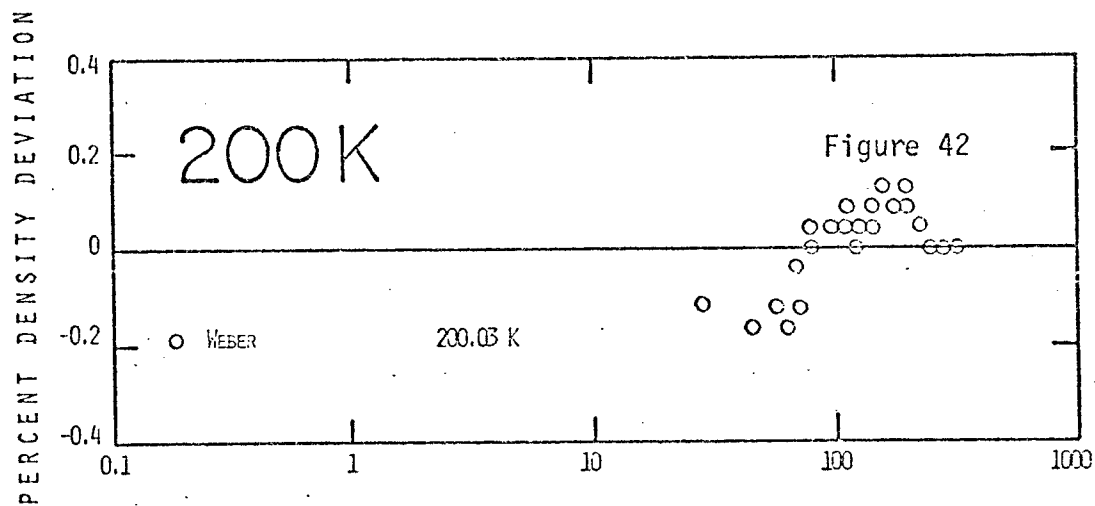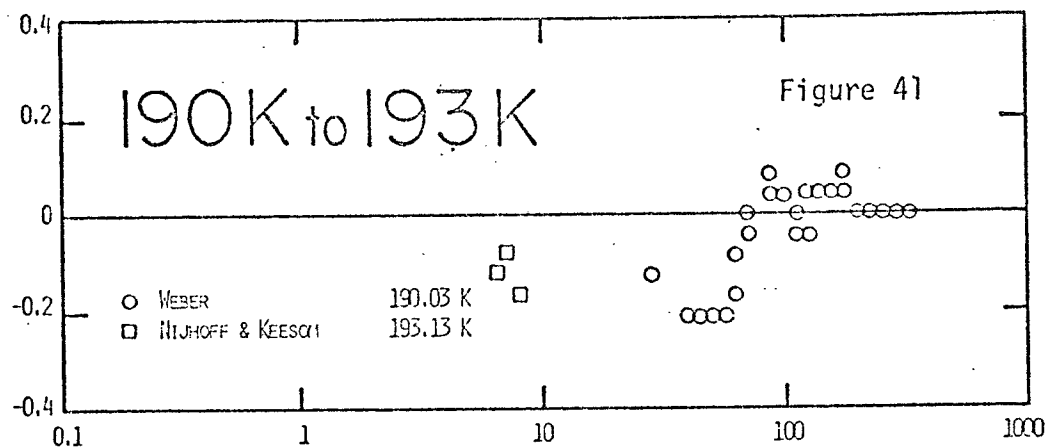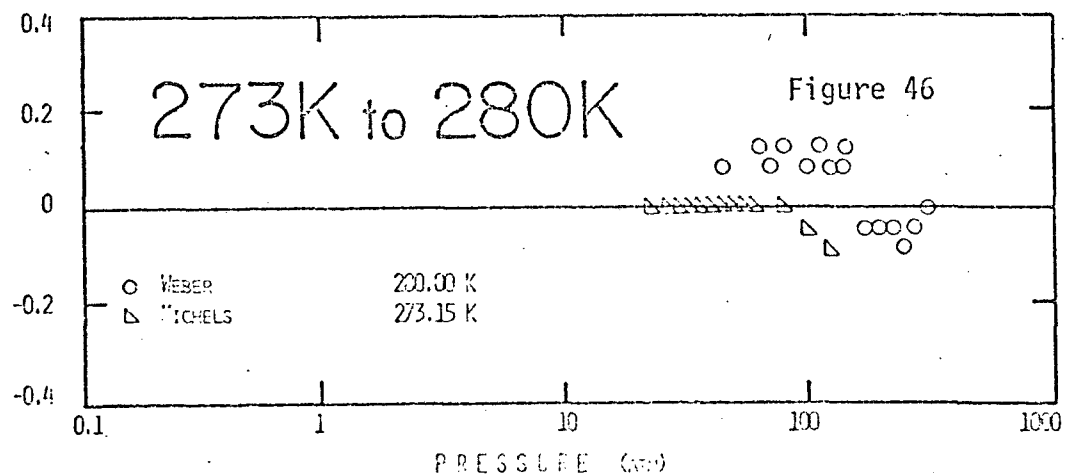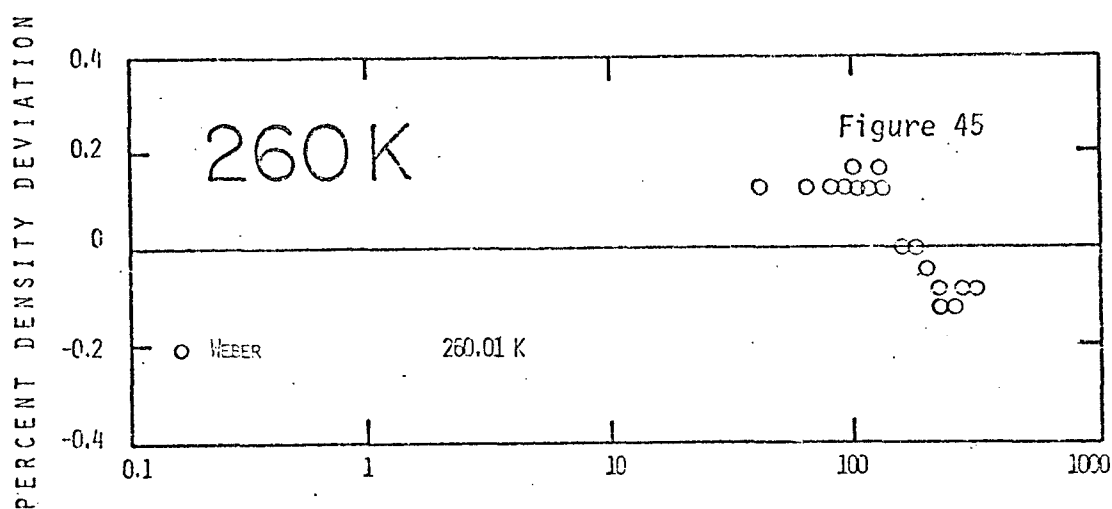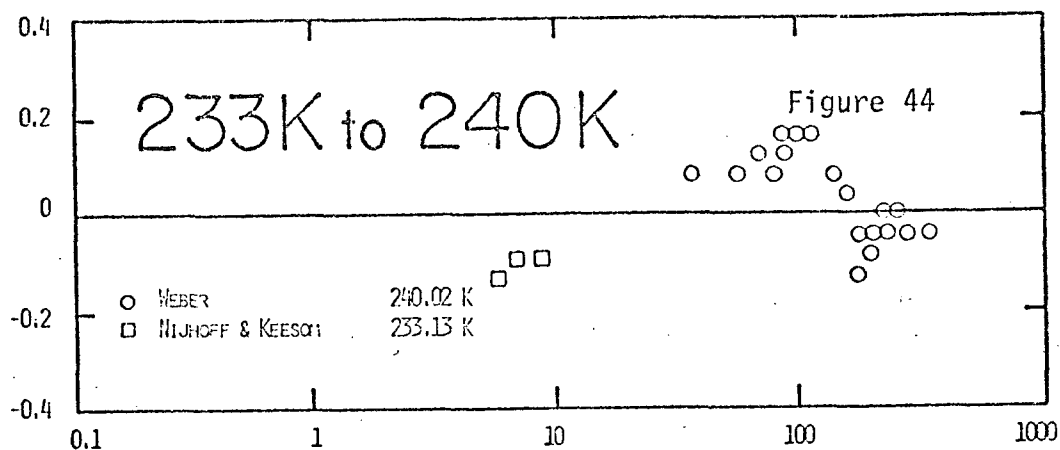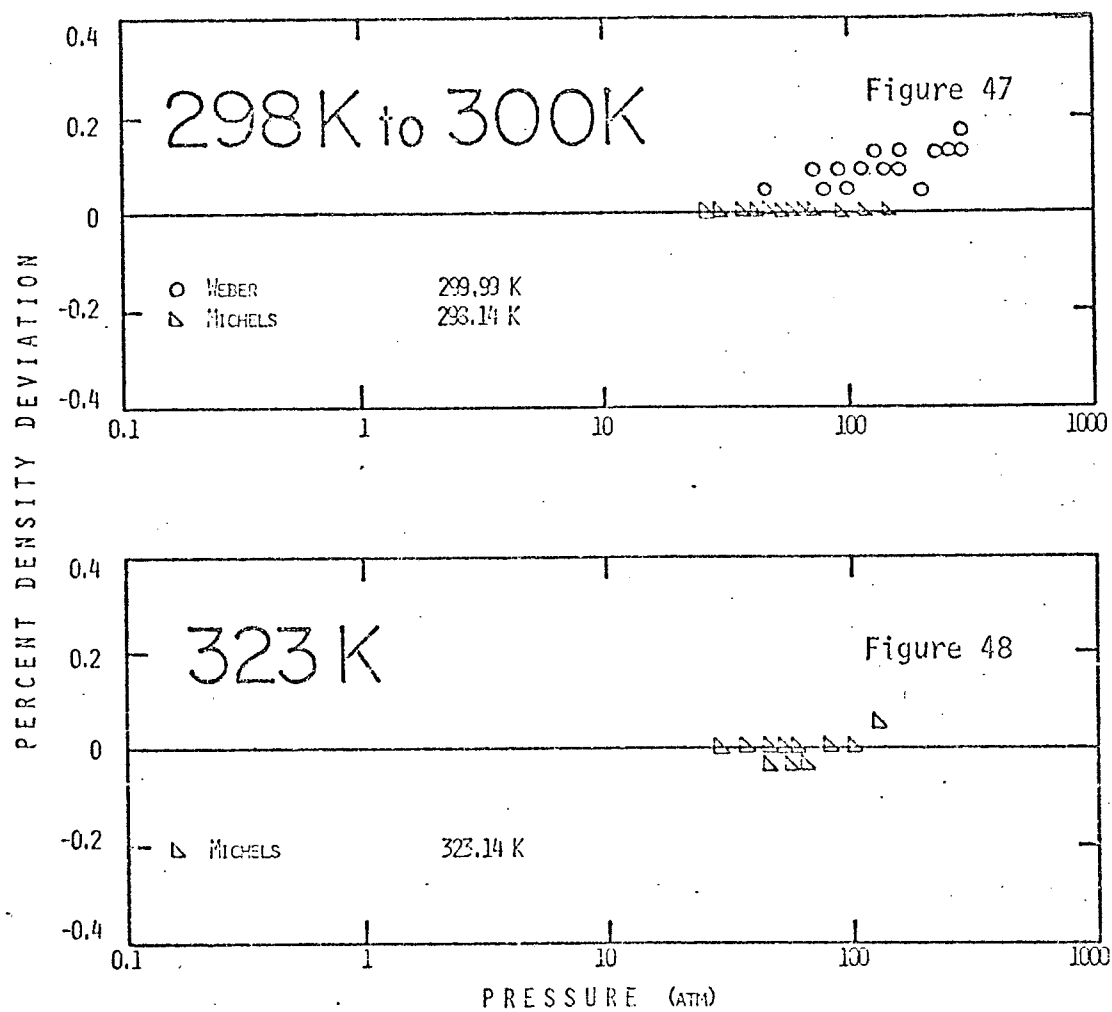Deviations in Density of Equation (2) from the Experimental Data of [U-1, O-2].

B. Thermodynamic Properties of Nitrogen

The need for a more detailed analysis of the functional form of the equation of state was needed, since a statistical analysis of the coefficients for nitrogen as determined for equation (2) showed that only about half of the coefficients of the terms employed in the equation had F-statistics high enough to indicate significance at the 95 percent confidence level. This analysis is now proceeding and is being accomplished by the use of a multiple-stepwise-regression program written by Mr. Garry L. Rose as an adjunct study to the work described in this report. The method of analysis being employed began by postulation of a 50-term polynomial equation of state containing terms in various powers of density up to ρ^{15} and including polynomials in temperature as coefficients and the exponential terms $e^{\gamma\rho^2}$. Successive fits of the equation are being performed with the term with the lowest F-value from the previous fit removed from the equation before each run. It is expected that this technique will result in an equation of state with from 25 to 35 terms, and with most terms statistically significant. The resultant equation will be examined by calculating derived properties, (i.e., enthalpy, entropy, and specific heats) for comparison to these quantities calculated from the equation reported in [7]. This study is in progress at the time of this report.

A review of the weighting techniques employed for the data used in the development of the equation of state is in progress. Prior weighting has been accomplished using the error-propagation formula as outlined in [3] with estimated experimental uncertainties in density. Preliminary results indicate that an improvement in the fit of the equation of state is apparent when weights are calculated directly from deviations in pressure from a prior fit of the same functional form. An exception noted in preliminary investigations is that deviations from data near the critical point appear to be larger using the latter weighting method.

The property calculation techniques described in [1] have been used in the development of generalized computer programs for the calculation of properties from the equation of state for nitrogen as well as for oxygen. Preliminary indications are that specific heat values calculated from the equation of state (2) exhibit large deviations from expected values in the vicinity of the critical point. Erratic behavior in specific heats calculated along isobars is evi-

dent in the liquid range for nitrogen indicating the need for further refinement of the equation of state in this region.

In summary, the equation of state (2) must be considered preliminary for this work, and further development is needed to insure more accurate values of the heat capacities calculated from the equation of state, particularly in the liquid region for nitrogen.

C. Volume Explicit Equation of State

The authors emphasize that the following equation is preliminary and request that it be used only for estimating temperature, pressure, and density in the range of applicability as defined in the following paragraphs. Users are advised to observe the accuracy estimates which follow.

To fill the need for a preliminary value of density to provide a first estimate for iterative density calculations using equation (2), a volume-explicit equation of state has been developed for oxygen using the P-ρ-T data of Weber [O-1] and Michels et al. [O-2]. This equation is valid only for the vapor for temperatures from 70 K to 323 K and pressures to 350 atm. The form of the equation is as follows,

$$
\begin{aligned}
V = \frac{RT}{P} &+ (G_1 T + G_2 + G_3/T + G_4/T^2) \\
&+ (G_5 T^2 + G_6 T + G_7 + G_8/T + G_9/T^2)\, P \\
&+ (G_{10} T + G_{11})\, P^2 + (G_{12} + G_{13}/T)\, P^3 \\
&+ P(G_{14}/T^2 + G_{15}/T^3 + G_{16}/T^4)\, e^{-0.00042 P^2} \\
&+ P^3(G_{17}/T^2 + G_{18}/T^3 + G_{19}/T^4)\, e^{-0.00042 P^2} \\
&+ P^5(G_{20}/T^2 + G_{21}/T^3 + G_{22}/T^4)\, e^{-0.00042 P^2}
\end{aligned}
$$

where: P is in atm., T in degrees K, and V in liters/mol.

The coefficients for this equation as determined by a fit to the data mentioned above are given in Table VII.

Table VII
Coefficients for Volume Explicit Equation of State for Oxygen

$G_1 = -0.626356236210567 \times 10^{-4}$	$G_{12} = 0.288909414495707 \times 10^{-8}$
$G_2 = 0.420325302822466 \times 10^{-1}$	$G_{13} = -0.756590342069606 \times 10^{-6}$
$G_3 = 0.930039707567091 \times 10^{1}$	$G_{14} = -0.327419883734544 \times 10^{3}$
$G_4 = -0.633366186967859 \times 10^{4}$	$G_{15} = 0.147356570339240 \times 10^{6}$
$G_5 = 0.297347348488700 \times 10^{-8}$	$G_{16} = -0.148388717945564 \times 10^{8}$
$G_6 = -0.315704935047603 \times 10^{-5}$	$G_{17} = 0.141067857045185$
$G_7 = 0.167077589933715 \times 10^{-2}$	$G_{18} = -0.698071127437031 \times 10^{2}$
$G_8 = -0.484651309742598$	$G_{19} = 0.826534646205043 \times 10^{4}$
$G_9 = 0.616394479750554 \times 10^{2}$	$G_{20} = -0.287912250216391 \times 10^{-4}$
$G_{10} = -0.297041470103540 \times 10^{-8}$	$G_{21} = 0.140246189667274 \times 10^{-1}$
$G_{11} = 0.753368564532407 \times 10^{-6}$	$G_{22} = -0.162991035903075 \times 10^{1}$

In general, the equation deviates from the data by ± 0.5 percent in the range 210 K to 323 K for pressures to 300 atm. The deviations are systematic particularly at high pressures. The accuracy of this equation is generally unacceptable for property calculation work and should be used only for initial estimates of property values. Using an estimated density calculated from this equation, the iterative solution of equation (2) may be expected to converge rapidly.

IV WORK PLANS FOR THE CONCLUSION OF THE PROJECT

Continuing studies of the functional form of the equation of state are expected to lead to a formulation which provides an acceptable statistical analysis of the fit with minimum deviations from the experimental data. Because the oxygen data of Weber [0-1] and Michels et al. [0-2] provide a precise representation of the P-ρ-T surface for the range of interest in this work, these data sets will be used for evaluation of the functional form of the equation of state and of fitting procedures. A parallel study will also be done for nitrogen using selected data sets for fitting.

A careful review of data weighting techniques for least squares fitting will be completed. The examination of various weighting procedures should result in an improved fit of the P-ρ-T data. In addition, it will be necessary to develop methods of weighting for use in simultaneous fitting as discussed below.

The methods of simultaneous fitting of P-ρ-T data and specific heat data will be employed in the determination of the equation of state for oxygen. The P-ρ-T data of Weber [0-1] and the C_v data of Goodwin and Weber [13] will be used for initial investigations of the methods to be used because of their demonstrated thermodynamic consistency. The techniques which are developed from these studies will then be applied to further studies of the equation of state for nitrogen.

In conjunction with the simultaneous fitting of heat capacity and P-ρ-T data, the criteria for phase equilibrium will be included in the fitting process, to investigate the effect of the procedure suggested by Bender [14] on the calculation of derived properties from the equation of state.

It is expected that the methods outlined here will result in an improved representation of the P-ρ-T surface with an accompanying improvement in calculated thermodynamic properties (e.g., entropy, enthalpy, heat capacities) for oxygen and nitrogen.

V BIBLIOGRAPHY

A. General References

1. Stewart, R.B., Ph.D. Thesis, University of Iowa (1966).

2. Coleman, T.C., and Stewart, R.B., Research Report No. 11, Engineering Experiment Station, University of Idaho (1970).

3. Coleman, T.C., and Stewart, R.B., paper presented to the XIII International Congress of Refrigeration, Washington, D.C. (1971).

4. McCarty, R.D. and Weber, L.A., National Bureau of Standards Tech. Note 384 (1971).

5. Kropschot, R.H., paper presented to MSC Cryogenics Symposium, NASA Manned Spacecraft Center, Houston (May 20, 1971).

6. Hall, W.J., McCarty, R.D. and Roder, H.M., NBS Report 9288 (Aug. 18, 1967).

7. Stewart, R.B. and Jacobsen, R.T., Final Report on Research Contract No. CST-962-5-69 to the Office of Standard Reference Data, National Bureau of Standards, U.S. Department of Commerce (1971).

8. Hilsenrath, J. Beckett, C.W., Benedict, W.S., Fano, L., Hoge, H.J., Masi, J.F., Nutall, R.K., Touloukian, Y.S., and Woolley, H.W., National Bureau of Standards Circular No. 564 (1955).

9. Baehr, H.D., Hartmann, H., Pohl, H.O., and Schomäcker, H., *Thermodynamische Funktionen idealer Gase für Temperaturen bis 6000 K*, Springer-Verlag, Berlin/Heidelberg (1968).

10. Hoge, H.J., Journal of Research of the National Bureau of Standards, 44, 321-45 (1950).

11. Myers, A.F., Jacobsen, R.T., and Stewart, R.B., paper presented to the XIII International Congress of Refrigeration, Washington, D.C. (1971).

12. Muijlwijk, R., Moussa, M.R., and van Dijk, H., Physica, 32, 805-22 (1966).

13. Goodwin, R.D., and Weber, L.A., Journal of Research of the National Bureau of Standards, 73A, 1-13 (1968).

14. Bender, E., paper in the *Proceedings of the Fifth Symposium on Thermophysical Properties*, C.F. Bonilla, editor, The American Society of Mechanical Engineers (Sept. 30 - Oct. 2, 1970).

B.   References to Nitrogen Properties

N-1   Amagat, E.H., Compt. Rend., 107, pp 522-25 (1888).
N-2   Bartlett, E.P., J. Am. Chem. Soc., 49, pp 1955-57 (1927).
N-3   Bartlett, E.P., Cupples, H.L., and Tremearne, T.H., J. Am. Chem. Soc., 50,
        pp 1275-88 (1928).
N-4   Bartlett, E.P., Hetherington, H.C., Kvalnes, H.M., and Tremearne, T.H.,
        J. Am., Chem. Soc., 52, pp 1363-73 (1930).
N-5   Benedict, M.J., J. Am. Chem. Soc., 59, pp 2224-33 (1937).
N-6   Benedict, M.J., J. Am. Chem. Soc., 59, pp 2233-42 (1937).
N-7   Canfield, F.B., Ph.D. Thesis, Rice University (1962).
N-8   Crain, R.W., Sonntag, R.E., and Van Wylen, G.J., Tech. Report on ORA Project
        06536, Univ. of Michigan (1965).
N-9   Friedman, A.S., Ph.D. Thesis, Ohio State (1950).
N-10 Gibbons, R.M., Cryogenics, 9, pp 251-60 (1969).
N-11 Goldman, K., Scrase, N.G., and Cockett, A.H., Private Communications (The
        British Oxygen Company) (1968).
N-12 Golubev, I.F., and Dobrovolskii, O.A., Gasovaia Promyshlen, 9, pp 43-47
        (1964).
N-13 Grilly, E.R. and Mills, R.L., Phys. Rev., 105, p 1140-45 (1957).
N-14 Hall, K.R., Ph.D. Thesis, University of Oklahoma (1967).
N-15 Heuse, W. and Otto, J., Ann.Physik, 2, pp 1012-30 (1929).
N-16 Holborn, L. and Otto, J., Z. Physik, 23, pp 77-94 (1924).
N-17 Holborn, L. and Otto, J., Z. Physik, 30, pp 320-28 (1924).
N-18 Kammerlingh Onnes, H.K., and van Urk, A.Th., Comm. Phys. Lab., Univ. Leiden,
        169-D (1924).
N-19 Malbrunot, P. and Vodar, B., C.R. Acad. Sci., Paris, Series A.B., 268B,
        No. 21 (1969).
N-20 Malbrunot, P., Doctoral thesis, l'Universite de Paris (1970); translation
        of Ch. 7-12, Angus, S., and Adalian, E., Paper PC/T11, IUPAC Thermo-
        dynamics Tables Project Centre, Imperial College, London (Dec. 1970).
N-21 Michels, A., Wouters, H. and DeBoer, J., Physica, 1, pp 587-94 (1934).
N-22. Michels, A., Wouters, H. and DeBoer, J., Physica, 3, pp 585-89 (1936).
N-23 Miller, J.E., Stroud, L., and Brandt, L.W., J. Chem. and Engr. Data, 5,
        No. 1 (1960).
N-24 Otto, J., Michels, A. and Wouters, H., Z. Physik, 35, pp 97-101 (1934).
N-25 Robertson, S.L. and Babb, S.E., J. of Chem. Phys., 50, pp 4560-64 (1969).
N-26 Saurel, J., J. des Recherches des CNRS, 42, pp 21-26 (1958).
N-27 Smith, L.B. and Taylor, R.S., J. Am. Chem. Soc., 45, pp 2107-24 (1923).
N-28 Streett, W.B. and Staveley, L.A.K., *Advances in Cryogenic Engineering*, Vol.
        13, pp 363-74, K.D. Timmerhaus, Editor, Plenum Press (1968).
N-29 Terry, M.J., Lynch, J.T., Bunclark, M., Mansell, K.R., and Staveley, L.A.K.,
        J. Chem. Thermodynamics, 1, pp 413-24 (1969).
N-30 Tsiklis, D.S., and Polyakov, E.V., Soc. Phys. Doklady, 12, No. 9 (1968).
N-31 Tsiklis, D.S., Akad. Nauk S.S.S.R. Doklady, 79, pp 289-90 (1951).
N-32 Van Itterbeek, A. and Verbeke, O., Physica, 26, pp 931-38 (1960).
N-33 Van Itterbeek, A. and Verbeke, O., Cryogenics, Vol. 2, No. 2, pp 79-80 (1961).
N-34 Verschoyle, T.T.H., Proc. Royal Soc., A111, pp 552-76 (1926).
N-35 Weber, L.A., J. Chem. Thermodynamics, Vol. 2, No. 6, 839-46 (1970).
N-36 Armstrong, G.T., J. of Research of N.B.S., 53, p 263 (1954).

C.   References to Oxygen Properties

0-1   Weber, L.A., National Bureau of Standards Report No. 9710, (June, 1968).

0-2   Michels, A., Schamp, H.W., and DeGraaff, W., Physica, 20, 1209-14 (1954).

0-3   Nijhoff, G.P., and Keesom, W.H., Communs. Phys. Lab. Univ. Leiden, No. 179b (1925).

0-4   Van Itterbeek, A., and Verbeke, O., Cryogenics, 1, No. 2, 77-80 (1960).